# THE VAPOR PRESSURE OF SOLID ARGON, CARBON MONOXIDE, METHANE, NITROGEN, AND OXYGEN FROM THEIR TRIPLE POINTS TO THE BOILING POINT OF HYDROGEN

A THESIS

Presented to

the Faculty of the Graduate Division

By

Leonard Mills Wylie

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemical Engineering

Georgia Institute of Technology

December 18, 1958

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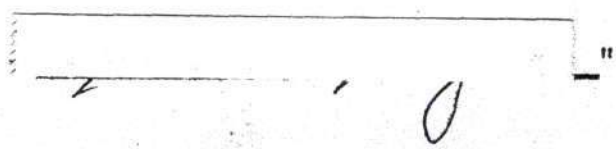

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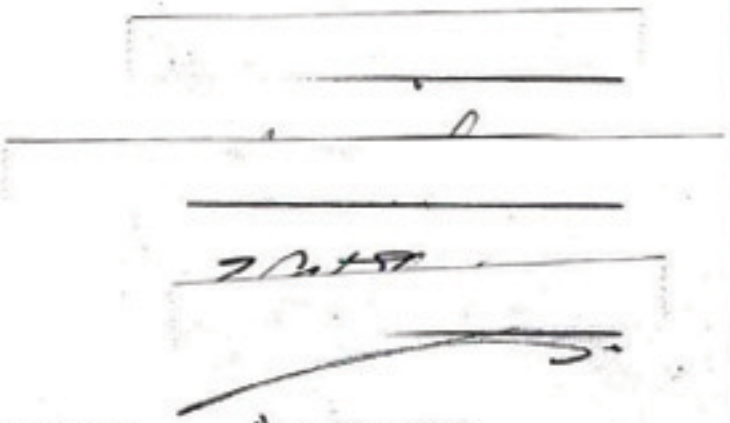

Date Approved by Chairman: Dec. 20, 1955

ACKNOWLEDGEMENT

I should like to express my appreciation to Dr. W. T. Ziegler for suggesting the problem, to the management of the Tennessee Corporation Research Laboratories for permitting the course of study, and, most of all, to my wife, Dorothy, for her encouragement and assistance.

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## SUMMARY

Experimentally determined vapor pressures of argon, carbon monoxide, methane, nitrogen, and oxygen in their solid states are scarce below their triple points. In particular, no reliable measured values are reported below 47.5°K. Reliable knowledge of the vapor pressures of these common substances is needed in industrial and theoretical approaches to liquefication and purification of gases at low temperatures. Generally, the only method of obtaining vapor pressures of these substances at temperatures much below their triple point down to the boiling point of hydrogen at 20.4°K. is by extrapolation of measured vapor pressure data or equations which are applicable for the measured temperature range. Development of vapor pressure equations, based on fundamental thermodynamic relationships and such data as are available in the literature and compared with reliable measured vapor pressures to test their validity, offers a more reliable source of vapor pressure data for the solids in the temperature ranges below the experimentally measured ranges.

By use of the exact fundamental thermodynamic relationship, the Clapeyron equation, and simplifying assumptions valid in the temperature and pressure range under consideration, the following general equation (see Fowler, Statistical Mechanics, 1936, p. 208) for calculating vapor pressure equations of solids has been earlier developed:

$$\ln p - \ln p_o = \frac{(\Delta H_s)_{t.p.}}{RT^2}\, dT \qquad (15)$$

$$+ \int_{T_{t.p.}}^{T} \frac{1}{RT^2} \left[ \int_{T_{t.p.}}^{T} (C_p^o - C_{p_{sol}})\, dT \right] dT$$

where

$p$ = vapor pressure of the solid at temperature T

$p_o$ = vapor pressure of the solid at the triple point, $T_{t.p.}$

$C_p^o$ = zero pressure heat capacity of the gas over the temperature range T to $T_{t.p.}$

$C_{p_{sol}}$ = heat capacity of the solid over the temperature range T to $T_{t.p.}$

$(\Delta H_s)_{t.p.}$ = heat of sublimation of the solid at the triple point

Reliable experimental values of $p_o$, $C_p^o$, and $C_{p_{sol}}$ from the literature are substituted in equation (15) to obtain an equation by which a value for $(\Delta H_s)_{t.p.}$ can be calculated using the reliable experimental vapor pressures and temperatures measured near the triple point. By substitution of the value of $(\Delta H_s)_{t.p.}$ in the equation, vapor pressure equation for the solid from its triple point to temperature T is obtained.

Equation (15) or analogous equations developed for such special cases as solids with transitions between T and $T_{t.p.}$ is used to develop the following vapor pressure equations for the solid forms of argon, carbon monoxide, nitrogen, methane, and oxygen:

Solid argon from its triple point at 83.78°K. to the boiling point of hydrogen at 20.4°K.

$$\log p(mm) = 6.1255 - \frac{410.78}{T} + 1.0608 \log T - 0.006555T \qquad (35)$$

Solid carbon monoxide from its triple point at 68.09°K. to the transition point at 61.57°K.

$$\log p(mm) = 6.9063 - \frac{414.78}{T} + 1.1499 \log T - 0.01264T \qquad (39)$$

and from the transition point at 61.57°K. to the boiling point at hydrogen at 20.4°K.

$$\log p(mm) = 2.4482 - \frac{418.44}{T} + 4.1340 \log T - 0.02599T \qquad (40)$$

Solid nitrogen from its triple point at 63.156°K to the transition point at 35.62°K.

$$\log p(mm) = + 6.9607 - \frac{372.37}{T} + 0.8655 \log T - 0.01029T \qquad (43)$$

and from the transition point at 35.62°K. to the boiling point of hydrogen at 20.4°K.

$$\log p(mm) = 0.6540 - \frac{357.92}{T} + 5.4630 \log T - 0.04490T \qquad (44)$$

Solid methane from its triple point at 90.66°K. to 21.35°K.

$$\log p(mm) = 2.0216 - \frac{478.51}{T} + 4 \log T - 0.2086T^{0.5624} \qquad (48)$$

Solid oxygen from its triple point at 54.363°K. to the first transition point at 43.8°K.

$$\log p\ (mm) = 12.3161 - \frac{473.71}{T} - 2.0431 \log T \qquad (53)$$

and from the first transition point at 43.8°K. to the second transition point at 23.9°K.

$$\log p(mm) = 1.9703 - \frac{447.50}{T} + 4.8018 \log T - 0.03398T \qquad (54)$$

and from the second transition point at 23.9°K. to the boiling point of hydrogen at 20.4°K.

$$\log p(mm) = -0.3882 - \frac{443.35}{T} + 6.7095 \log T - 0.05258T \qquad (55)$$

The vapor pressures calculated from these equations are in good agreement with experimental vapor pressures from the literature. The change in temperature required to make the vapor pressures calculated from these equations equal to the experimental vapor pressures is about $\pm$ 0.1°K.

Since these equations are based on fundamental thermodynamic relationships applicable over the termperature range considered and on reliable experimental data in regions near the triple points where the accuracy is high, it is believed that these vapor pressure equations for the individual substances yield values for the vapor pressure of the solids with greater reliability than could be obtained by extrapolation of experimental vapor pressure data to lower temperatures.

These equations have certain limitations arising from the uncertainties in the heat of sublimation, the failure to include the difference between the enthalpy of the saturated vapor and the ideal gas, and the uncertainties in the thermal data for the condensed phases. It is

believed that these uncertainties may lead to errors of as much as a factor of two in the computed vapor pressures near 20°K. This uncertainty is equivalent to approximately ± 0.2°K.

# LIST OF SYMBOLS

| | |
|---|---|
| $(\Delta H_s)_o$ | Heat of sublimation at 0°K. |
| $(\Delta H_s)_{t.p.}$ | Heat of sublimation at the triple point |
| $(\Delta H_s)_{trans}$ | Heat of sublimation at the transition point |
| $(\Delta H_v)_{t.p.}$ | Heat of vaporization at the triple point |
| $(\Delta H_f)_{t.p.}$ | Heat of fusion at the triple point |
| $(\Delta H_v)_{b.p.}$ | Heat of vaporization at boiling point |
| T | Temperature, °K. |
| $C_p^o$ | Heat capacity of the gas at zero pressure |
| $C_{p_{sol}}$ | Heat capacity of the condensed phase |
| $(Cp)_1$ | Variable part of the heat capacity of the gas |
| $(C_p)_o$ | Constant part of the zero pressure heat capacity of the gas |
| i | Chemical constant |
| V | Volume |
| g | Gas |
| p | Pressure |
| $p_o$ | Vapor pressure at the triple point |
| R | 1.98719 calories per gram-mole °K. |
| $C_{Sat.\ liq.}$ | Heat capacity of the saturated liquid |
| B | Second virial coefficient |

# CHAPTER I

## INTRODUCTION

The Problem.--Experimentally determined values for the vapor pressures of argon, carbon monoxide, methane, nitrogen, and oxygen in their solid states are scarce below their triple points. The accompanying brief review of references illustrates the scarcity of data for these substances in this region.

Dokoupil, van Soest, and Swenker (1) have measured the vapor pressure of solid nitrogen down to 42.1°K. Aoyama and Kanda (2) have measured the vapor pressure of both solid oxygen and nitrogen down to 36°K. and 30.8°K., respectively. The values of Aoyama and Kanda are not thought to be accurate by other experimenters such as Hoge (3) because of questionable pressure measurements. In the case of oxygen, other than Aoyama and Kanda, only Hoge (3) has published measured vapor pressures below the triple point. Hoge considers his three values of the vapor pressure of oxygen measured slightly below the triple point not as reliable as his measurement of the vapor pressure at the triple point because of possible condensation in the tube leading to the manometer.

Smoothed values of the vapor pressure of methane down to 48.16°K. have been reported by Tickner and Lossing (4). Liang (5) has corrected the values obtained by Tickner and Lossing for the thermal transpiration effect.

The lowest recorded vapor pressure measurements on carbon monoxide are those of Verschoyle (6) which extend down to 54.21°K. Clayton and Giaugue (7) have calculated an equation for the vapor pressure of solid carbon monoxide below 61.55°K. based on calorimetric data. Born (8) has measured the vapor pressure of argon down to 65.49°K.

The vapor pressures of the solid states of these materials in the temperature range below 47.5°K. down to the boiling point of hydrogen are either of questionable reliability or not available in the literature. Vapor pressures in this temperature range must be obtained by extrapolation of the experimental equations developed for the region near the triple points, by estimation procedures, or calculated with fundamental equations and measured data from the literature.

The National Bureau of Standards (9) (10) has made a critical compilation of existing published and unpublished data on the thermal properties of gases which included argon, carbon monoxide, nitrogen, and oxygen. Vapor pressure equations based on the best experimental data were developed for the areas covered by the measured values. The constants of the Antoine equation and smoothed values of the vapor pressure of methane are tabulated. Armstrong, Brickwedde, and Scott (11) critically reviewed the vapor pressure data of methane in the literature and made a very small adjustment in the vapor pressure equation of the National Bureau of Standards (10).

The ever increasing industrial and basic research interest in liquefaction and purification of gases at low temperatures indicates the need for extending our knowledge of the thermal properties of such

common gases as these to as low a temperature as possible.

Purpose of the Research.--The purpose of this research was to use such data as are available in the literature and fundamental thermodynamic relationships to develop valid vapor pressure equations for calculating the vapor pressures of these substances in the solid state from their triple points to the boiling point of hydrogen at 20.4°K. The validity of the vapor pressure equations was to be determined by comparison with existing experimentally measured values from the literature. It was felt that the development of equations for calculating the vapor pressures of these gases in their solid states in a form convenient for application over a temperature range not presently covered by experimentation would be a valuable contribution to the literature.

# CHAPTER II

## THEORETICAL

The Vapor Pressure of Classical Thermodynamics.--Fowler (12) has discussed the vapor pressure equation of classical thermodynamics. He developed an equation of the following form.

$$\log p = -\frac{(\Delta H_s)_o}{RT} + \frac{(Cp)_o}{R} \log T \qquad (1)$$

$$+ \int_o^T \frac{dT}{RT^2} \int_o^T \left[(Cp)_l - (Cp)_{sol}\right] dT + i$$

where

$p$ = vapor pressure of the condensed phase

$(\Delta H_s)_o$ = heat of sublimation at $0^oK$.

$i$ = the chemical constant

$(Cp)_l$ = variable part of the heat capacity of the gas

$(Cp)_o$ = constant part of the zero pressure heat capacity of the gas

$(Cp)_{sol}$ = heat capacity of the condensed phase

In deriving equation (1) Fowler assumed the first and second laws of thermodynamics and that the vapor is and ideal gas. The difference between $(Cp)_{sol}$ at zero pressure or one atmosphere or for the sequence of natural vapor pressures were considered so trivial that they could be ignored; therefore, $(Cp)_{sol}$ for the condensed phase at some standard pressure, usually one atmosphere, was used.

Development of the Vapor Pressure Equation.--We begin with the fundamental Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H_s}{T(V_g - V_s)} \tag{2}$$

where $\Delta H_s$, the heat of sublimation, is equal to the difference between the enthalpy of the gas and the enthalpy of the solid at the pressure and temperature of the system. For the special case to be considered, namely a solid with vapor pressure less than one atmosphere, we will assume that the vapor phase is an ideal gas.

$$V_g = \frac{RT}{p} \tag{3}$$

Since the volume of gas, $V_g$, is so very much greater than the volume of the solid, $V_s$, we will neglect $V_s$.

$$V_s = 0 \tag{4}$$

Finally we will write

$$\Delta H_s = f(T) \tag{5}$$

which assumes that the enthalpy of the solid is independent of the pressure.

Substituting equations (3), (4), and (5) in (2) gives

$$d \ln p = \frac{\Delta Hs}{RT^2} dT \tag{6}$$

where the right hand side is a function of temperature only.

At the triple point we find

$$(\Delta H_s)_{t.p.} = (\Delta H_v)_{t.p.} + (\Delta H_f)_{t.p.} \tag{7}$$

At any temperature lower than the triple point we find a particular value of $\Delta H_s$ and in general may write

$$d\Delta H_s = \left(\frac{\partial \Delta H_s}{\partial T}\right)_p dT + \left(\frac{\partial \Delta H_s}{\partial p}\right)_T dp \tag{8}$$

$$= \left(\frac{\partial \Delta H_g}{\partial T}\right)_p - \left(\frac{\partial \Delta H_{sol}}{\partial T}\right)_p dT$$

$$+ \left(\frac{\partial \Delta H_g}{\partial p}\right)_T - \left(\frac{\partial \Delta H_{sol}}{\partial p}\right)_T dp \tag{9}$$

We have assumed $\left(\frac{\partial \Delta H_g}{\partial p}\right)_T = 0$, $\left(\frac{\partial \Delta H_{sol}}{\partial p}\right)_T = 0$, and $\left(\frac{\partial \Delta H_g}{\partial T}\right)_p = C_p^o = f(T)$;

therefore,

$$\frac{d\Delta H_s}{dT} = C_p^o - C_{p_{sol}} \tag{10}$$

Integrating equation (10) gives

$$\Delta H_s = \int (C_p^o - C_{p_{sol}})dT + C \tag{11}$$

or

$$(\Delta H_s)_{t.p.} - (\Delta H_s)_T = \int_T^{T_{t.p.}} (C_p^o - C_{p_{sol}})dT \tag{12}$$

whence

$$(\Delta H_s)_T = (\Delta H_s)_{t.p.} - \int_T^{T_{t.p.}} (C_p^o - C_{p_{sol}})dT \tag{13}$$

We note that the data required to evaluate $(\Delta H_s)_T$ are $(\Delta H_s)_{t.p.}$, $C_p^o$, and $C_{p_{sol}}$ over the temperature range $T_{t.p.}$ to T.

Substituting equation (13) in equation (6) gives

$$d \ln p = \frac{1}{RT^2} \left[ (\Delta H_s)_{t.p.} + \int_{T_{t.p.}}^{T} (C_p^o - C_{p_{sol}})dT \right] dT \tag{14}$$

Integrating between the limits $(p_o, T_{t.p.})$ and $(p,T)$ where $p_o$ is equal to the vapor pressure at the triple point we obtain

$$\ln p - \ln p_o = \int_{T_{t.p.}}^{T} \frac{(\Delta H_s)_{t.p.}}{RT^2}\, dT \qquad (15)$$

$$+ \int_{T_{t.p.}}^{T} \frac{1}{RT^2} \left[ \int_{T_{t.p.}}^{T} (C_p^o - C_{p_{sol}})\, dT \right] dT$$

Equation (15) is derived from the Clapeyron equation, which is an exact fundamental equation, and therefore should be exact if the stated assumptions are valid. Equation (15) is the general equation for the vapor pressure of a solid from its triple point to the temperature T with no transitions in the temperature range stated. Special cases of this general equation are discussed in Chapter III.

We note that the vapor pressure of the solid below the triple point can be determined from equation (15) if $p_o$, $C_p^o$, $C_{p_{sol}}$, and $(\Delta H_s)_{t.p.}$ are known. If the vapor pressures at the triple points of the gases under consideration have all been measured experimentally and the heat capacities of the solid and the zero pressure heat capacities of the gases over the temperature range are available, $(\Delta H_s)_{t.p.}$, can be evaluated. The accuracy of the vapor pressure determined from equation (15) is dependent on the accuracy of the experimental vapor pressure, $p_o$, at the triple point and at least one accurate vapor pressure measurement of the solid below the triple point as well as the heat capacity of the solid and gas as a function of the T used to determine the heat of sublimation, $(\Delta H_s)_{t.p.}$, at the triple point. In some cases the experimentally determined heat capacity of the solid, $C_{p_{sol}}$, may actually be the heat capacity of the solid measured under its own vapor pressure rather than at constant pressure; however, the contribution to the enthalpy of the solid should be very minor (12).

$(\Delta H_s)_{t.p.}$ may also be evaluated by correcting the experimentally determined heat of vaporization of the gas at some temperature above the triple point to its value at the triple point and combining the value so obtained with the experimental heat of fusion according to equation (7).

# CHAPTER III

## DEVELOPMENT OF VAPOR PRESSURE EQUATIONS

Vapor Pressure Equations for Solids with Linear Heat Capacity Expressions.-- Equation (15) is the general equation for the vapor pressure of the solid. The final form of the equation derived after integration will, of course, vary with the type or form of equations which best fit the heat capacity of the gas in the solid state and the zero pressure heat capacity of the gas over the temperature range considered.

For the special case of a substance for which the heat capacity of the solid can be represented by a linear equation of the form

$$C_{p_{sol}} = a + bT \tag{17}$$

and the zero pressure heat capacity of the gas, $C_p^o$, is constant, we may substitute the appropriate expression in equation (15), perform the indicated integration and obtain

$$\ln p = -\frac{(\Delta H_s)_{t.p.} - C_1}{RT} + \frac{(C_p^o - a)}{R} \ln T - \frac{bT}{2R} + \left[-C_2 + C_3 + \ln p_o\right] \tag{18}$$

where

$$C_1 = (C_p^o - a)(T_{t.p.}) - \frac{b}{2}(T_{t.p.}^2)$$

$$C_2 = \frac{1}{R}\,(C_p^o - a)\,\ln T_{t.p.} - \frac{bT_{t.p.}}{2R}$$

$$C_3 = \frac{(\Delta H_s)_{t.p.} - C_1}{RT_{t.p.}}$$

$p_o$ = vapor pressure at the triple point

$p$ = vapor pressure

Vapor Pressure Equations for Solids with Parabolic or Hyperbolic Heat Capacity Expressions and a Constant Zero Pressure Heat Capacity.--For the special case of a gas for which the heat capacity of the solid can be represented by an equation for a parabolic or hyperbolic curve of the form

$$C_p = a\,T^b \tag{19}$$

and the zero pressure heat capacity of the gas, $C_p^o$, is constant, we may substitute these expressions in equation (15) perform the indicated integration and obtain

$$\ln p = -\frac{(\Delta H_s)_{t.p.} - C_1}{RT} + \frac{C_p^o}{R}\ln T - \frac{aT^b}{(b^2+b)R} + \left[-C_2 + C_3 + \ln p_o\right] \tag{20}$$

where

$$C_1 = \left(C_p^{\circ} T_{t.p.} - \frac{aT_{t.p.}^{b+1}}{b+1}\right)$$

$$C_2 = \frac{C_p^{\circ} \ln T_{t.p.}}{R} - \frac{aT_{t.p.}^{b}}{R(b^2+b)}$$

$$C_3 = \frac{(\Delta H_s)_{t.p.} - C_1}{RT_{t.p.}}$$

$p_o$ = vapor pressure at the triple point

$p$ = vapor pressure

Vapor Pressure Equations for Solids with Transitions Between Their Triple Points and 20.4°K.--Equation (15) is the general equation for the vapor pressure of a solid gas from its triple point to the temperature T with no crystalline transitions in the temperature range stated. Where one transition occurs between the triple point and 20.4°K., the general equation developed after substituting the proper heat capacity expressions is valid only down to the transition point. At the transition point Solid I is in equilibrium with and changes to Solid II with evolution of the heat of transition. At the transition point and below until another transition is encountered, a general vapor pressure equation for Solid II valid from the transition temperature, $T_{trans}$, to a temperature T less than $T_{trans}$ and analogous to equation (15) is applicable. We may write

$$\ln p - \ln p_{trans} = \int_{T_{trans}}^{T} \frac{(\Delta H_s)_{trans\ sol\ II}}{RT^2}\, dT \qquad (21)$$

$$+ \int_{T_{trans}}^{T} \frac{I}{RT^2} \left[ \int_{T_{trans}}^{T} (C_p^o - C_{p_{sol\ II}})dT \right] dT$$

where

$p_{trans}$ = the vapor pressure of Solid I (the high temperature form) and Solid II (the low temperature form) at the transition temperature

$C_{p_{sol\ II}}$ = the heat capacity of Solid II over the temperature range considered

$(\Delta H_s)_{trans\ Sol\ II}$ = the heat of sublimation of Solid II at the transition point.

We note that all of the assumptions made in developing equation (15) apply to equation (21). To obtain data for evaluation of $(\Delta H_s)_{trans}$, we may write

$$(\Delta H_s)_{trans\ Sol\ II} = (\Delta H)_{trans} + (\Delta H_s)_{trans\ Solid\ I} \qquad (22)$$

where

$(\Delta H_s)_{trans\ Sol\ II}$ = heat of sublimation of Solid II at the transition point

$(\Delta H)_{trans}$ = heat of transition of Solid II to Solid I

$(\Delta H_s)_{trans\ Sol\ I}$ = heat of sublimation of Solid I at the transition point

The final form of the vapor pressure equation developed from equation (21) will vary as equation (15) did with the type of equation which fits the heat capacity data best.

We may develop analogous vapor pressure equations for solids with more than one transition between the triple point and 20.4°K. similarly.

Vapor Pressure Equations of Solids Based on Experimental Data at and Above the Triple Point.--In the absence of accurate vapor pressure measurements below the triple point we must rely on the experimental data at the triple point and above to evaluate $(\Delta H_s)_{t.p.}$ in equation (15).

We may evaluate $(\Delta H_s)_{t.p.}$ by correcting the experimentally determined heat of vaporization of the gas in the liquid state at its normal boiling point to the temperature of the triple point. One gram mole of the gas in the liquid state may be evaporated at constant temperature and at one atmosphere pressure absorbing energy equal to $(\Delta H_v)_{b.p.}$, the heat of vaporization at the normal boiling point. We now expand the gas isothermally and reversibly from one atmosphere to zero pressure where the change in enthalpy is equal to $H^o$(b.p.) -H(b.p., 1 atm.). The gas at constant pressure is cooled from the boiling point to the triple point losing energy equal to $\int_{b.p.}^{t.p.} C_p^o \, dT$. We compress the gas isothermally and reversibly from zero pressure to the normal triple point pressure where the change in enthalpy is equal to H(t.p.,t.p.press.) -$H^o$(t.p.). We now condense the gas to the liquid state at the triple point temperature and pressure removing heat equal to $(\Delta H_v)_{t.p.}$ and then add heat keeping the pressure at its equilibrium value for the temperature until we reach the normal boiling point having added energy equal to $\int_{t.p.}^{b.p.} C_{\text{Sat. liq.}} \, dT$. We have completed the cycle and may write for the complete cycle

$$\Sigma H = 0 \tag{23}$$

or

$$(\Delta H_v)_{b.p.} + \left[H^\circ(b.p.) - H(b.p., 1 \text{ atm.})\right] g + \int_{b.p.}^{t.p.} C_p^\circ \, dT \tag{24}$$

$$+ \left[H(t.p., \text{ t.p.pressure}) - H^\circ(t.p.)\right] g - (\Delta H_v)_{t.p.}$$

$$+ \int_{t.p.}^{b.p.} C_{\text{Sat. liq.}} \, dT = 0$$

Therefore

$$(\Delta H_v)_{t.p.} = (\Delta H_v)_{b.p.} + \int_{b.p.}^{t.p.} \left(C_p^\circ - C_{\text{Sat. liq.}}\right) dT \tag{25}$$

$$+ \left[H^\circ(b.p.) - H(b.p., 1 \text{ atm.})\right] g$$

$$+ \left[H(t.p., t.p.\text{pressure}) - H^\circ(t.p.)\right] g$$

An equation similar to equation (25) may be written for any other temperature for which $\Delta H_v$ is known.

The bracketed expressions in equation (25) are the corrections for gas imperfection which we can obtain from the following relationships. Let us write the virial equation in the form

$$p = \frac{RT}{V} + \frac{B}{V^2} \tag{26}$$

or

$$pV = RT + \frac{B}{V} \tag{27}$$

then, very nearly,

$$pV = RT + \frac{Bp}{RT} \tag{28}$$

or

$$V = \frac{RT}{p} + \frac{B}{RT} \tag{29}$$

Differentiating equation (29) at constant pressure with respect to temperature we obtain

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \frac{1}{RT}\frac{dB}{dT} - \frac{B}{RT^2} \tag{30}$$

Equation (30) can be substituted in the thermodynamic equation

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{31}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{R}\frac{dB}{dT} \quad \frac{2B}{RT} \tag{32}$$

We may evaluate the expression for the correction for gas imperfection by substituting the slope of the plot of experimental values of the second virial coefficient as a function of the temperature in equation (32)

$$\int_0^p \left(\frac{\partial H}{\partial p}\right)_T dp = H(p,T) - H^o(T) = -\frac{1}{R}\frac{dB}{dT}(p) + \frac{2B}{RT}(p) \tag{33}$$

# CHAPTER IV

## VAPOR PRESSURE EQUATIONS OF THE GASES

### Method of Presentation

General Discussion.--Vapor pressure equations for the solid phases of argon, carbon monoxide, methane, nitrogen, and oxygen from their triple points to the boiling point of hydrogen at 20.4°K. are developed in this chapter. Data discussed in the individual sections on each gas and used in the development of the vapor pressure equations are tabulated in the appendix.

Tables of the vapor pressures of the solids calculated at five degree intervals, including the triple and transition points down to the boiling point of hydrogen at 20.4°K., are included. Plots of the log p(mm) of the gases as a function of the reciprocal of the absolute temperature are also included.

Sample calculations for the complete development of the vapor pressure equations of argon and oxygen are presented in the appendix to illustrate the procedure for calculating the vapor pressures of solids using the equations developed in Chapter III.

The experimental vapor pressure data from the literature are compared with our equations to test their validity.

### Vapor Pressure of Argon from Its Triple Point to the Boiling Point of Hydrogen at 20.4°K.

Review of the Literature.--The National Bureau of Standards (13) has

made a critical compilation of the measured experimental vapor pressure data of solid argon and developed an empirical equation for the temperature range from 83.78°K., the triple point, to 65°K. The triple point accepted was that of Frank and Clusius (14). Experimental vapor pressure data of Crommelin (15) (16), Born (8), Ramsay and Travers (17), and Holst and Hamburger (18) were used in the NBS analysis. The work of Born (8) is questionable. Since the analysis of the data by the National Bureau of Standards, Clark, Din, Robb, Michels, Wassenaar, and Zwietering (19) have reported new values for the vapor pressure, considered to be as accurate as those of Hoge (3) for oxygen, and have developed an equation for the vapor pressure of solid argon from the triple point to 70°K. which represents the data of Crommelin (16) equally well.

In developing a vapor pressure equation, we will use the triple point pressure of 516.8 mm. of Hg. and triple point at 83.78°K. established by the NBS (13).

The only specific heat measurements found in the literature on the solid from the triple point to 20.4°K. were those of Clusius and Frank (20) which are represented by the equation

$$C_p = 2.86 + 0.0600T - 6.8\times10^5\ T^{-4.35} \qquad (34)$$

Equation (34) which we fitted to the data by the method of Lipka (21) reproduces the experimental values within an average of $\pm$ 1.5 per cent. The treatment of this form of the heat capacity equation is explained in the following section and the sample calculations in the appendix.

The zero pressure heat capacity of argon is constant, since it is a monatomic gas. The zero pressure heat capacity was taken from the compilation of the NBS (13) where $C_p^o/R$ is given as 2.5000. The value of

R, 1.98719 calories per mole per $^{o}K.$, was that used by the National Bureau of Standards (13).

The Vapor Pressure Equation for Argon.--We note that sufficient experimental data are available to evaluate the heat of sublimation at the triple point, $(\Delta H_s)_{t.p.}$. The zero pressure heat capacity is constant and the heat capacity of the solid is essentially linear with a small correction for deviation at one end. In Chapter III, equation (18) was developed for a solid with a linear heat capacity, equation (17), and a constant zero pressure heat capacity. Equation (20) was developed for a solid with a parabolic or a hyperbolic heat capacity expression, equation (19). We write the specific heat equation, equation (34), in a form analogous to the specific heat equations (17) and (19); therefore, the last term becomes $+CT^d$. Substituting this expression for $C_{p_{sol}}$ in equation (15) and performing the indicated operations, we obtain a modified form of equation (18) which contains the added term, $-\frac{CT^d}{R(d^2+d)}$ and where

$$C_1 = C_p^o T_{t.p.} - aT_{t.p.} - \frac{bT^2_{t.p.}}{2} - \frac{CT^{d+1}_{t.p.}}{d+1}$$

$$C_2 = \frac{(C_p^o - a)}{R} \ln T_{t.p.} - \frac{bT_{t.p.}}{2R} - \frac{CT^d_{t.p.}}{R(d^2+d)}$$

$$C_3 = \frac{(\Delta H_s)_{t.p.} - C_1}{RT_{t.p.}}$$

The vapor pressure equation of argon will have the form of equation (18) with the added term.

Substituting the values of $p_o$, $C_p^o$, and $C_{p_{sol}}$ in equation (15) and performing the indicated operations, we determine $(\Delta H_s)_{t.p.}$ for the experimental data of Clark, Din, Robb, Michels, Wassenaar, and Zwietering (19) and Crommelin (16) which are in good agreement. The second measurement of Crommelin was given the greatest weight in the critical compilation of the National Bureau of Standards (13). The calculated values of $(\Delta H_s)_{t.p.}$ are tabulated in Table 1 and Table 2.

Table 1. Calculated Values of $(\Delta H_s)_{t.p.}$
Based on Experimental Data of Crommelin (16)

| T°K. | Pressure in mm Hg. | $(\Delta H_s)_{t.p.}$ |
|---|---|---|
| 81.80 | 394.29 | 1861 |
| 78.58 | 251.01 | 1809 |
| 77.56 | 208.8 | 1873 |
| 75.91 | 163.5 | 1837 |
| 72.19 | 84.56 | 1861 |
| 70.95 | 67.83 | 1853 |
| 69.38 | 51.19 | 1835 |
| 67.84 | 38.30 | 1822 |

Table 2. Calculated Values of $(\Delta H_s)_{t.p.}$
Based on Experimental Data of Clark, Din, Robb, Michels, Wassenaar, and Zwietering (19)

| T°K. | Pressure in mm Hg. | $(\Delta H_s)_{t.p.}$ |
|---|---|---|
| 70 | 57.7 | 1835 |
| 72 | 83.5 | 1839 |
| 74 | 118.5 | 1842 |
| 76 | 165.1 | 1845 |
| 78 | 226.1 | 1849 |
| 80 | 304.8 | 1856 |
| 82 | 405.0 | 1869 |

Giving equal weight to the values obtained from both sets of data, the average value of $(\Delta H_s)_{t.p.}$ is 1846 ± 14 calories per gram-mole.

Substituting this value of $(\Delta H_s)_{t.p.}$ in the equation which was derived from equation (15), we obtain for the vapor pressure equation of argon from the triple point at 83.78°K. to 20.4°K.

$$\log p(mm) = 6.1255 - \frac{410.78}{T} + 1.0608 \log T - 0.006555T \qquad (35)$$

The derivation of equation (35) is shown in the appendix as a sample calculation.

Comparison of the vapor pressure calculated from equation (35) with the experimental values of Crommelin (16), show that the equivalent temperature change required to obtain equal vapor pressures is less than $\pm$ 0.1°K. with the exception of the experimental measurement at 67.84°K. for which + 0.15°K. is required. The data of Clark, Din, Robb, Michels, Wassenaar and Zwietering (19) check to within an equivalent temperature of $\pm$ 0.1°K. at all points. The empirical equation developed by the NBS (13) checks within an equivalent temperature of less than $\pm$ 0.1°K. with the exception that near 65°K. the deviation is less than + 0.2°K. The experimental data of Born (8) require an equivalent temperature of greater than - 0.20°K. over the entire range.

The deviation of the observed vapor pressure of argon from the vapor pressure calculated from equation (35) is plotted as a function of the absolute temperature in Figure 1. The deviation, $P_{observed}-P_{calculated}/P_{calculated}$, is expressed as per cent.

It is concluded that equation (35) yields results for the vapor pressure of solid argon which are reliable to about $\pm$ 0.5 mm Hg. at 65°K.

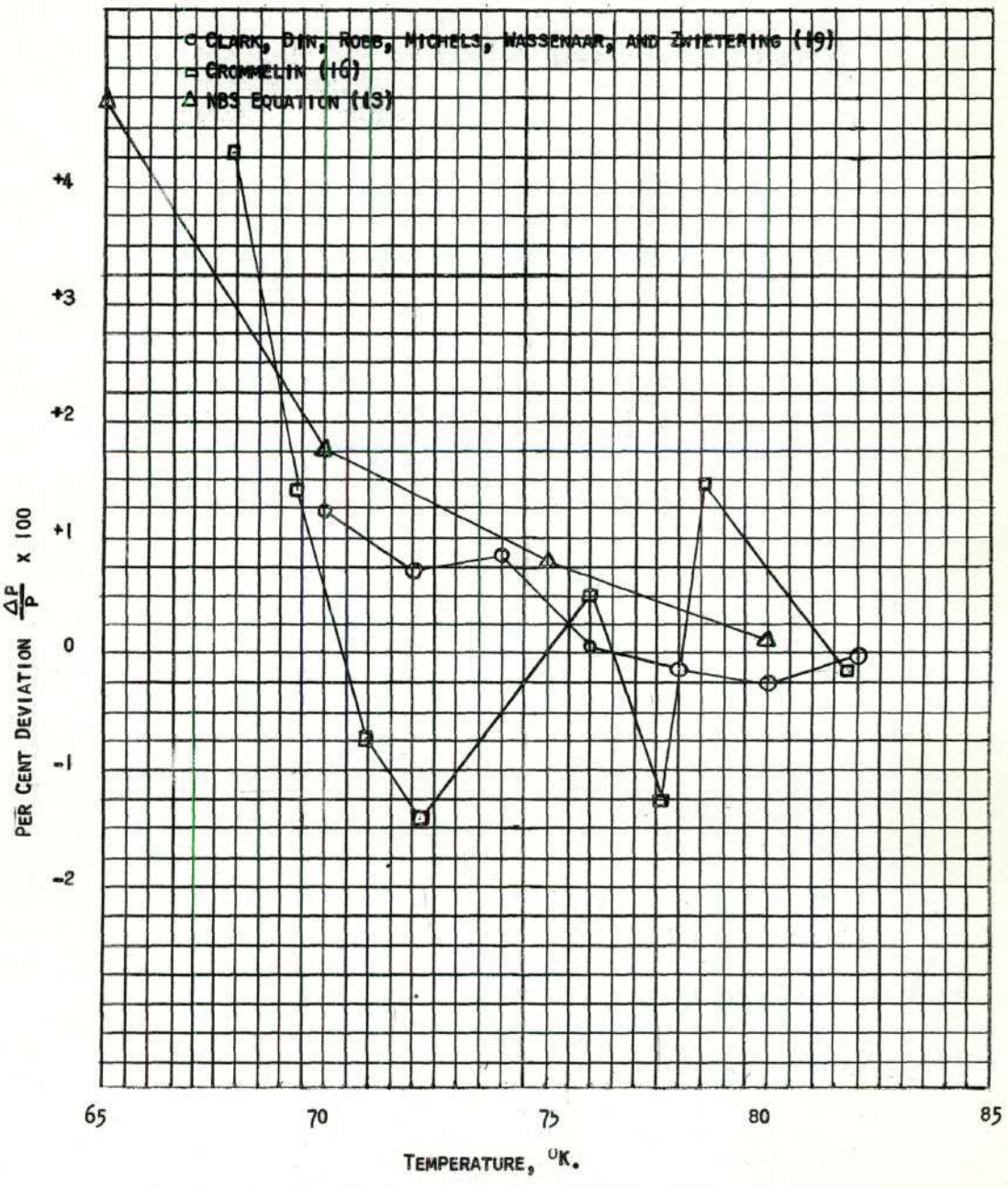


FIGURE 1. PER CENT DEVIATION OF OBSERVED VAPOR PRESSURE OF ARGON FROM THAT CALCULATED USING EQUATION (35).

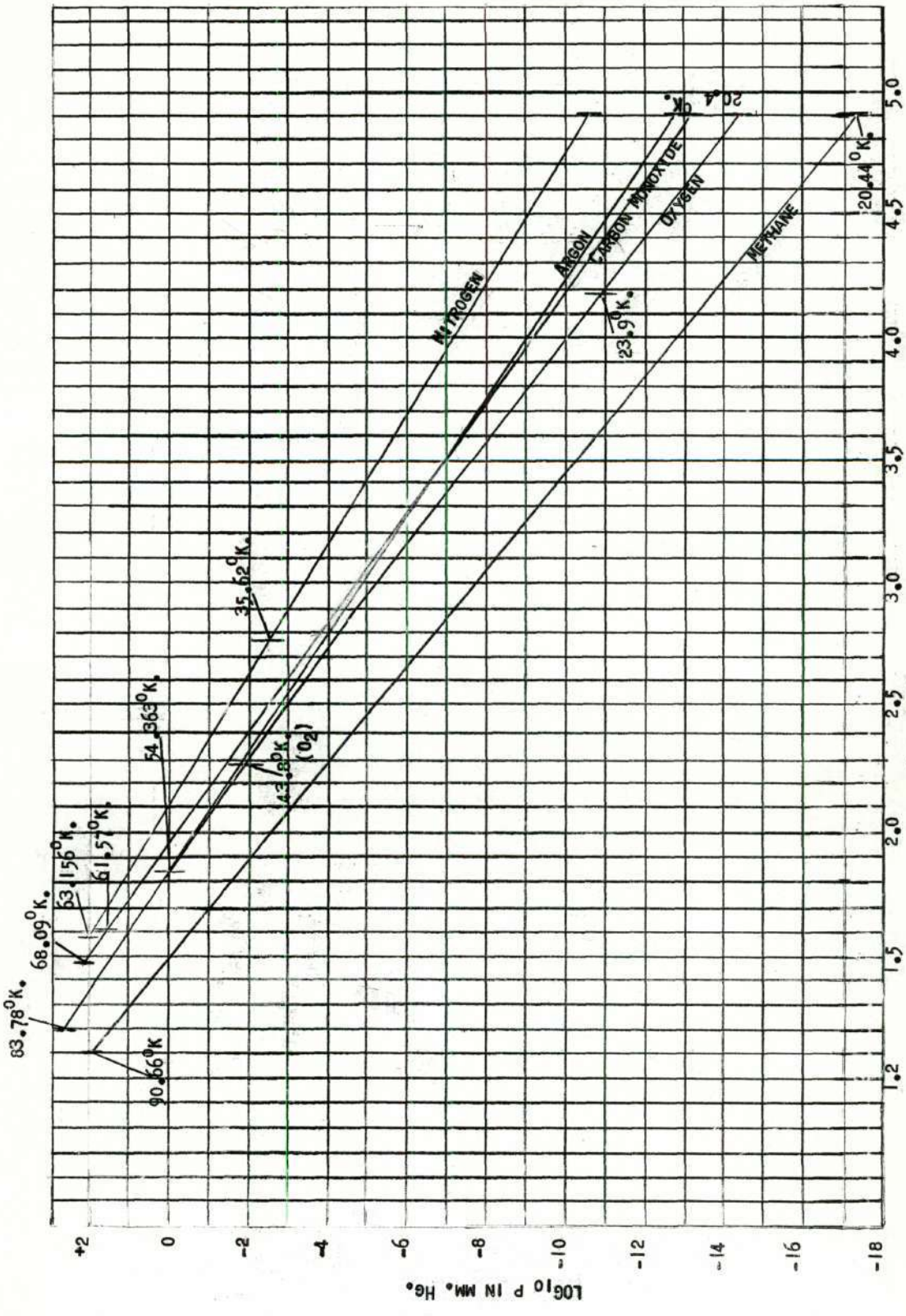


FIGURE 2. PLOT OF LOGARITHM OF VAPOR PRESSURE OF THE GASES AGAINST THE RECIPROCAL OF THE ABSOLUTE TEMPERATURE

The vapor pressures of solid argon calculated from equation (35) are tabulated in Table 3. A plot of log p(mm) as a function of the reciprocal of the absolute temperature, $1/T^{\circ}K.$, is shown in Figure 2. The triple point of argon and the boiling point of hydrogen are marked on the plot by vertical lines and the value of the absolute temperature in $^{\circ}K.$

Table 3. Vapor Pressure of Solid Argon

| Temperature, $^{\circ}K.$ | Pressure, mm. Hg. |
|---|---|
| 83.78 (triple point) | 516.8 |
| 80 | 305.6 |
| 75 | 139.9 |
| 70 | 57.0 |
| 65 | 20.1 |
| 60 | 5.9 |
| 55 | 1.4 |
| 50 | $2.4 \times 10^{-1}$ |
| 45 | $2.9 \times 10^{-2}$ |
| 40 | $2.0 \times 10^{-3}$ |
| 35 | $6.3 \times 10^{-5}$ |
| 30 | $6 \times 10^{-7}$ |
| 25 | $1 \times 10^{-9}$ |
| 20. 4 | $2 \times 10^{-13}$ |

Vapor Pressure of Carbon Monoxide from Its Triple Point to the Boiling of Hydrogen at $20.4^{\circ}K.$

Review of the Literature.--The National Bureau of Standards (22) has made a critical compilation of the measured experimental vapor pressure of solid carbon monoxide and developed empirical vapor pressure equations applicable from the triple point at $68.09^{\circ}K.$ to the transition point at $61.57^{\circ}K.$ and below the transition point to $54^{\circ}K.$ Experimental vapor pressure data of Clayton and Giauque (7), Crommelin, Bijleveld, and Brown (23), Verschoyle (6), and Clusius and Teske (24) were compared and the systematic differences appeared to be due primarily to the use

of different temperature scales.

Clayton and Giauque (7) developed the following vapor pressure equation for solid carbon monoxide from the transition point at 61.57°K. to 20°K.

$$\log p(\text{mm}) = -\frac{418.2}{T} + 4.127 \log T \qquad (36)$$

$$+ 1.47365 - 0.02623T$$

Clayton and Giauque (7) used their calorimetric data, equation (31), and the Berthelot equation to develop equation (36).

Stull (25) has plotted the vapor pressure data available in the literature and tabulated the temperature and vapor pressure read at fixed points on the curve.

In the development of our vapor pressure equation we will use the triple point temperature of 68.09°K., transition point temperature of 61.57°K., vapor pressure at the triple point of 115.3 mm., and vapor pressure at the transition point of 28.1 mm. as established by the NBS compilation (22).

Experimental heat capacity data for solid carbon monoxide have been reported by Clayton and Giauque (7), Eucken (26), Clusius (27) and Kaischew (28). The data of Clusius agree quite well with that of Clayton and Giauque. The largest deviation is well below 20°K. The average deviation is about 3 per cent. The data of Eucken do not agree as well while the data of Kaischew agree with that of Clayton and Giauque to within an average of less than two per cent. The data of Clayton and Giauque will be used to develop our vapor pressure equation for solid

carbon monoxide. The heat capacity from the triple point to the transition point is represented by the equation

$$C_p = 4.67 + 0.116T \tag{37}$$

and from the transition point to 20.4°K. by

$$C_p = -1.26 + 0.238T \tag{38}$$

Equation (37) reproduces the experimental data to within an average of ± 0.1 per cent while equation (38) reproduces the data to within an average of ± 2.2 per cent. Both equation (37) and (38) were fitted to the data by the method of Lipka (21).

The zero pressure heat capacity was compiled by the National Bureau of Standards (22) based on calculations of Goff and Gratch (29).

The heat of transition of solid carbon monoxide at 61.57°K. measurements of Clayton and Giauque (7), Clusius (27), and Kaischew (28) are in very close agreement while the value of Eucken (26) is considerably lower. The heat of transition used was 151.8 calories per gram-mole reported by Clayton and Giauque (7).

The Vapor Pressure Equations for Solid Carbon Monoxide.--We note that sufficient experimental data are available to evaluate $(\Delta H_s)_{t.p.}$. The zero pressure heat capacity is considered constant and the heat capacity of the two solid forms of carbon monoxide is linear. The vapor pressure equation for solid carbon monoxide from the triple point at 68.09°K. to the transition point at 61.57°K. will have the form of equation (18) as will the vapor pressure equation for solid carbon monoxide below the transition point to 20°K. after substitution of the proper values in equation (21) and perform-

ing the indicated operations.

We determine the heat of sublimation at the triple point, $(\Delta H_s)_{t.p.}$ for the experimental data of Clayton and Giauque (7) as tabulated in Table 4.

Table 4. Calculated Values of $(\Delta H_s)_{t.p.}$
Based on Experimental Data of Clayton and Giauque (7)

| T°K | Pressure in mm. Hg. | $(\Delta H_s)_{t.p.}$ |
|---|---|---|
| 62.22 | 32.75 | 1789 |
| 63.30 | 42.30 | 1780 |
| 64.31 | 52.83 | 1786 |
| 65.28 | 65.46 | 1771 |
| 66.12 | 77.69 | 1787 |
| 67.02 | 93.25 | 1795 |

We substitute the average value of $(\Delta H_s)_{t.p.}$, 1785 ± 6 calories per gram-mole, in equation (18) and we obtain the vapor pressure equation for solid carbon monoxide over the range 68.09°K. to 61.57°K.

$$\log p(mm) = 6.9063 - \frac{414.78}{T} + 1.1499 \log T - 0.01264T \qquad (39)$$

We substitute the proper values in equation (21) and equation (22) and obtain the vapor pressure equation for solid carbon monoxide over the range 61.57°K. to 20.4°K.

$$\log p(mm) = 2.4482 - \frac{418.44}{T} + 4.1340 \log T - 0.02599T \qquad (40)$$

Comparison of the vapor pressures calculated by equations (39) and (40) with the experimental values and equation (37) obtained by Clayton and Giauque (7), shows that the temperature change required to obtain

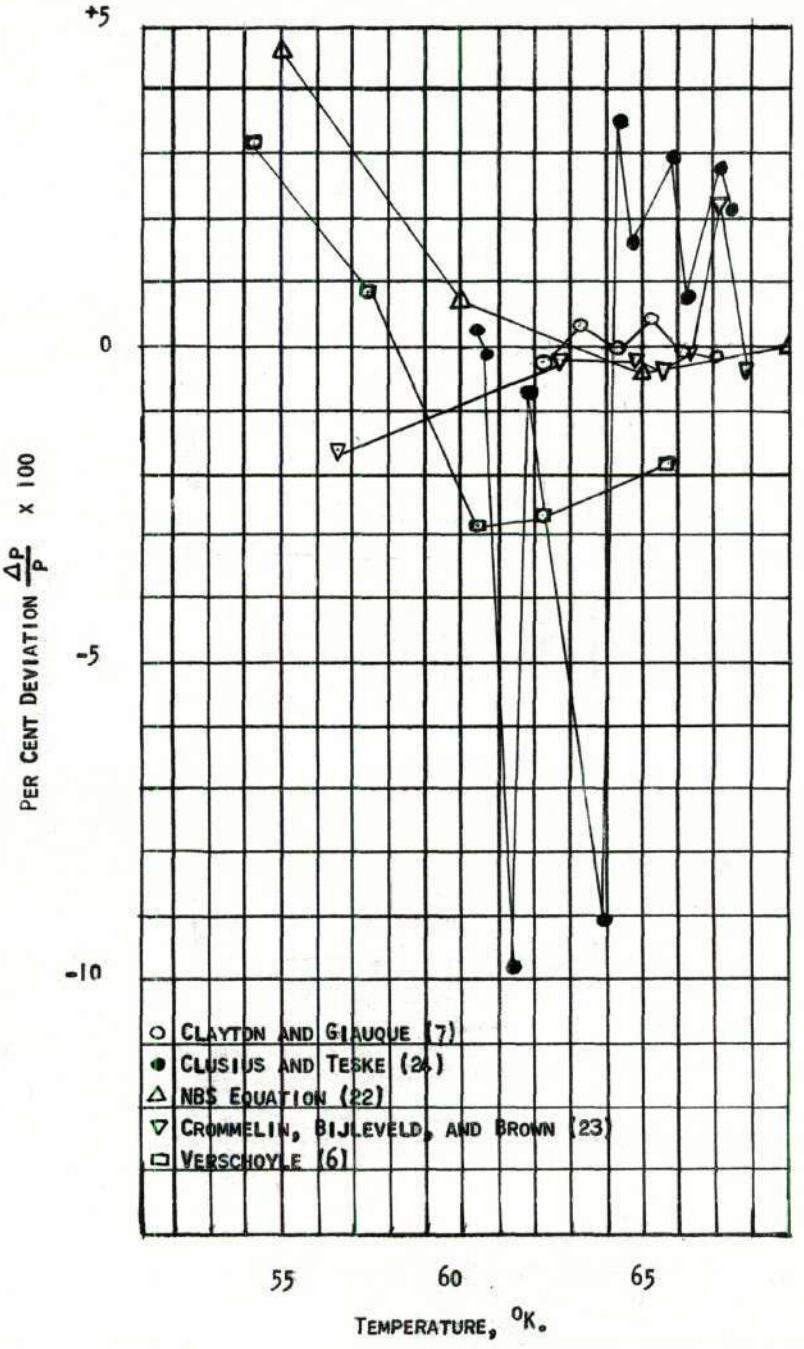


FIGURE 3. PER CENT DEVIATION OF OBSERVED VAPOR PRESSURE OF CARBON MONOXIDE FROM THAT CALCULATED USING EQUATIONS (39) AND (40).

equal vapor pressures is less than ± 0.05°K. The equation of Clayton and Giauque (7) is, therefore, equally as good as our equation. The data of Verschoyle (6) require a temperature change of less than ± 0.15°K. over the temperature range he measured. The data of Clusius and Teske (24) check to within an equivalent temperature of less than ± 0.2°K. with the exception of one point which is greater than - 0.4°K. The data of Crommelin, Bijleveld, and Brown (23) check to within an equivalent temperature of less than ± 0.11°K. over the entire range. The empirical equation developed by the NBS (22) checks to within an equivalent temperature of less than ± 0.03°K. over the range from the triple point to 60°K. and deviates by less than + 0.15°K. at 55°K. The deviation of the observed vapor pressure of carbon monoxide from the vapor pressure calculated from equations (39) and (40) is plotted as a function of the absolute temperature in Figure 3. The deviation, $P_{observed}-P_{calculated}/P_{calculated}$, is expressed as per cent. The values for the vapor pressure of solid carbon monoxide are uncertain by about ± 0.1°K. This corresponds to ± 0.5 mm at 60°K.

The vapor pressure of solid carbon monoxide calculated from equations (39) and (40) are tabulated in Table 5. A plot of log p(mm) as a function of the reciprocal of the absolute temperature, 1/T°K., is shown in Figure 2. The triple point and transition point of carbon monoxide and the normal boiling point of hydrogen are marked on the plot with vertical lines and the absolute temperature in °K.

Table 5. Vapor Pressure of Solid Carbon Monoxide

| Temperature, °K. | P, in mm. Hg. |
|---|---|
| 68.09 (triple point) | 115.3 |
| 65.00 | 61.4 |
| 61.57 (transition) | 28.1 |
| 60.00 | 18.4 |
| 55.00 | 4.0 |
| 50.00 | $6.4 \times 10^{-1}$ |
| 45.00 | $6.5 \times 10^{-2}$ |
| 40.00 | $3.7 \times 10^{-3}$ |
| 35.00 | $9.3 \times 10^{-5}$ |
| 30.00 | $7 \times 10^{-7}$ |
| 25.00 | $7 \times 10^{-10}$ |
| 20.40 | $7 \times 10^{-14}$ |

Vapor Pressure of Nitrogen from Its Triple Point to the Boiling Point of Hydrogen at 20.4°K.

Review of the Literature.--The National Bureau of Standards (30) has made a critical compilation of the measured experimental vapor pressure of solid nitrogen and developed an empirical equation for the range from 63.156°K., the triple point, to 52°K. Experimental vapor pressure data of Keesom and Bijl (31), Giauque and Clayton (32), von Siemens (33), and Henning (34) were used in the NBS compilation. The triple point was established by the NBS compilation as 63.156°K. and the solid transition point as 35.62°K. Stull (25) has plotted the vapor pressure data available in the literature and tabulated the temperature and vapor pressure read at fixed points on the curve. Dokoupil, van Soest, and Swenker (1) have reported approximately determined values of the vapor pressure.

Experimental heat capacity data for solid nitrogen have been reported by Giauque and Clayton (32) and Clusius (27) whose results were in good

agreement with Keesom and Onnes (35) and Eucken (26) below the transition point and the triple point. The average deviation of the heat capacity data of Giauque and Clayton (32) and Clusius (27) is about one per cent from the triple point to the transition point and about three per cent below the transition point. The data of Giauque and Clayton will be used to develop our vapor pressure equation for solid nitrogen. The heat capacity from the triple point to the solid transition point 35.62°K., is represented by the equation

$$C_p = 5.236 + 0.09420T \qquad (41)$$

and from the transition point to 20.4°K. by

$$C_p = -3.90 + 0.411T \qquad (42)$$

Equation (41) reproduces the experimental data to within an average of $\pm$ 0.34 per cent while equation (42) reproduces the data to within an average of $\pm$ 2.4 per cent. Both equation (41) and (42) were fitted to the data by the method of Lipka (21).

The zero pressure heat capacity has been compiled by the National Bureau of Standards (30) and is tabulated in the appendix. The zero pressure heat capacity is essentially constant over the temperature range considered.

The heat of transition has been measured by Giauque and Clayton (32), Clusius (27), and Eucken (26). The value of 54.71 calories per gram-mole obtained by Giauque and Clayton will be used in our calculation.

The Vapor Pressure Equations for Solid Nitrogen.--We note that sufficient experimental data are available to evaluate the heat of sublimation at the triple point, $(\Delta H_s)_{t.p.}$. The zero pressure heat capacity is essentially

constant and the heat capacity of solid nitrogen is linear from the triple point to the solid transition point and linear below the transition point. The vapor pressure equation for solid nitrogen from the triple point to the solid transition point will have the form of equation (18). Below the solid transition point to 20.4°K., the vapor pressure equation of nitrogen will have the form of equation (18) when the proper values are substituted in equation (21) and the indicated operations are performed.

We determine the heat of sublimation at the triple point, $(\Delta H_s)_{t.p.}$ for the experimental data of Giauque and Clayton (32) as tabulated in Table 6.

Table 6. Calculated Values of $(\Delta H_s)_{t.p.}$

Based on Experimental Data of Giauque and Clayton (32)

| T°K. | Pressure mm.Hg. | $(\Delta H_s)_{t.p.}$ Clayton and Giauque |
|---|---|---|
| 54.783 | 12.73 | 1624 |
| 55.875 | 17.10 | 1626 |
| 56.930 | 22.44 | 1631 |
| 57.850 | 28.40 | 1627 |
| 58.741 | 35.26 | 1628 |
| 59.550 | 42.85 | 1620 |
| 60.670 | 55.26 | 1621 |

We substitute the average value of $(\Delta H_s)_{t.p.}$, 1625 ± 4 calories per gram-mole, in equation (18) and obtain the vapor pressure equation for solid nitrogen from the triple point of nitrogen at 63.156°K. to the solid transition at 35.62°K.

$$\log p(mm) = + 6.9607 - \frac{372.37}{T} + 0.8655 \log T - 0.01029T \qquad (43)$$

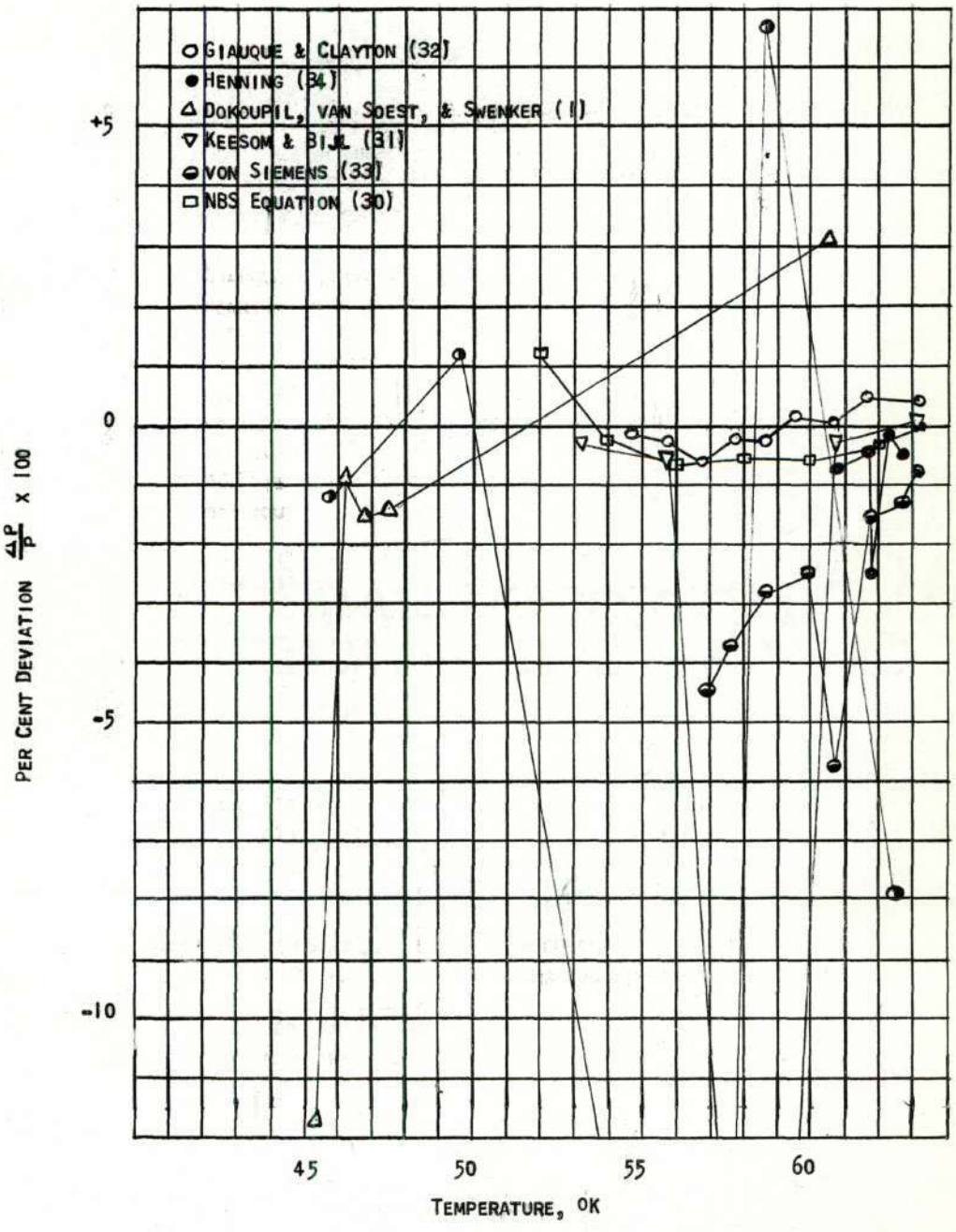


FIGURE 4. PER CENT DEVIATION OF OBSERVED VAPOR PRESSURE OF NITROGEN FROM THAT CALCULATED USING EQUATION (43).

We substitute the proper values in equation (21) and equation (22) and obtain the vapor pressure equation for solid nitrogen from the solid transition at 35.62°K. to the boiling point of hydrogen at 20.4°K.

$$\log p(\text{mm}) = 0.6540 - \frac{357.92}{T} + 5.4630 \log T - 0.04490T \qquad (44)$$

The vapor pressures calculated by equations (43) and (44) agree with the experimental vapor pressure data of Keesom and Bijl (31), Giauque and Clayton (32), Henning (34), and von Siemens (33) to less than ± 0.1°K. in equivalent temperature with the exception of the last two values of von Siemens which require an equivalent temperature change of - 0.13°K. The nitrogen temperature data of von Siemens (33) were adjusted to the NBS temperature scale by applying the correction Hoge (3) applied to bring oxygen temperature data into agreement. The empirical equation developed by the National Bureau of Standards (30) checks to within an equivalent temperature of ± 0.05°K.

The deviation of the observed vapor pressure of nitrogen from the vapor pressure calculated from equations (43) and (44) is plotted as a function of the absolute temperature in Figure 4. The deviation $P_{observed} - P_{calculated}/P_{calculated}$, is expressed as per cent.

The values for the vapor pressure of solid nitrogen are uncertain by about ± 0.1°K. This corresponds to ± 1.09 mm Hg. at 60°K.

The vapor pressure of solid nitrogen calculated from equations (43) and (44) is tabulated in Table 7. A plot of log p(mm) as a function of the reciprocal of the absolute temperature, 1/T°K., is shown in Figure 2. The

triple point and solid transition point of nitrogen and the normal boiling point of hydrogen are marked on the plot with vertical lines and the value of the absolute temperature in °K.

Table 7. Vapor Pressure of Solid Nitrogen

| Temperature, °K. | P, in mm. Hg. |
|---|---|
| 63.156 (triple point) | 94.0 |
| 60 | 47.4 |
| 55 | 13.5 |
| 50 | 2.9 |
| 45 | $4.5 \times 10^{-1}$ |
| 40 | $4.2 \times 10^{-2}$ |
| 35.62 (transition) | $3.0 \times 10^{-3}$ |
| 30 | $2.8 \times 10^{-5}$ |
| 25 | $7 \times 10^{-8}$ |
| 20.4 | $2 \times 10^{-11}$ |

Vapor Pressure of Methane from Its Triple Point to the Boiling Point of Hydrogen at 20.4°K.

Review of the Literature.--The National Bureau of Standards (10) has developed an equation for the vapor pressure of solid methane from the triple point to 77.65°K. Based on their own measurements and an exacting study of available data in the literature, Armstrong, Brickwedde, and Scott (11) adjusted the National Bureau of Standards (10) equation slightly to bring the triple point vapor pressure to 87.50 mm. Hg. and the temperature to 90.66°K. The adjusted equation is as follows:

$$\log p(\text{mm}) = 7.6950 - 532.20/(T + 1.842) \qquad (45)$$

Henning and Stock (36) measured the vapor pressure of methane below the triple point to 80.27°K. and developed a vapor pressure equation for solid methane. Karwat (37) measured the vapor pressure down to 76.89°K. and developed a vapor pressure equation for the range 75°K. to 90.5°K.

Tickner and Lossing (4) measured the vapor pressure of solid methane from 77.66°K. to 48.16°K. Liang (5) corrected the values of Tickner and Lossing for the thermal transpiration effect. Stull (25) has surveyed the literature and extrapolated data down to 1 mm. Hg. Freeth and Verschoyle (38) have also measured the vapor pressure of solid methane.

The triple point was established by Armstrong, Brickwedde, and Scott (11) at 90.66°K. and 87.50 mm. of mercury.

Clusius (27) found a solid transition point for methane at 20.44°K. The heat capacity change before and after the transition is quite pronounced for a small change in the temperature. Because of the extreme difficulty in handling the area near the transition point and between the transition point and the boiling point of hydrogen at 20.4°K., the equation will be developed to extend down to 21.35°K. and extrapolated to 20.4°K.

The specific heat of solid methane has been determined by Frank and Clusius (39) who, however, failed to observe the phase change at 20.44°K. The data of Eucken and Karwat (40) extended to 28.65°K. The data of Clusius (27) extend below the boiling point of hydrogen and include the solid transition point at 20.44°K. The specific heat data of Frank and Clusius (39) and Clusius (27) were combined and are represented by the equation

$$C_p = 0.8389T^{0.5624} \qquad (46)$$

Equation (46) fitted to the data by the method of Lipka (21) reproduces all the data to an average of $\pm$ 2.3 per cent; the data of Eucken and Karwat (40) is reproduced to an average of $\pm$ 1.4 per cent.

The methane molecule is a nonlinear polyatomic molecule with 15 degrees of freedom. The translation and rotation of the molecule account for six

degrees of freedom leaving nine vibrational degrees of freedom. The vibrational contributions to the zero pressure heat capacity were calculated using the vibration frequencies of Sponer (42) and the vibrational contributions to thermodynamic properties tabulated in Hougen and Watson (43) and found to be negligible. Electronic contributions are also of no consequence at these low temperatures. The contribution to the zero pressure heat capacity of translation and rotation both classically excited is 6R/2. The equation for the zero pressure heat capacity of the gas, therefore, is

$$C_p^o = \frac{3}{2} R + \frac{3}{2} R + R \qquad (47)$$

MacDougall (44) has considered the possible non-classical nature of the rotational contribution to the heat capacity of methane. Such an effect is to be expected at low temperatures. His calculations show that the effect is not appreciable above 40°K. and is at a maximum at about 25°K. If we neglect the non-classical rotational contributions to the zero pressure heat capacity, the effect on the vapor pressure calculated is very small until the very lowest temperatures are reached.

The Vapor Pressure Equation for Methane.--We note that sufficient data are available to evaluate the heat of sublimation at the triple point, $(\Delta H_s)_{t.p.}$. The zero pressure heat capacity is taken to be constant and the heat capacity of the solid is fitted by a parabolic heat capacity expression; therefore, the vapor pressure expression will have the form of equation (20).

We substitute the values of $p_o$, $C_p^o$, $C_{p_{sol}}$ in equation (15), perform the indicated operations, and determine $(\Delta H_s)_{t.p.}$ for the experimental vapor pressure data of Karwat (37) and Henning and Stock (36). These data are used, although the data of Tickner and Lossing (4) corrected for the thermal

transpiration effect by Liang (5) is available, because the effect is not appreciable in the temperature and pressure range covered by the data used. The calculated values of $(\Delta H_s)_{t.p.}$ are tabulated in Table 8.

Table 8. Calculated Values of $(\Delta H_s)_{t.p.}$
Based on Experimental Data of Karwat (37) and Henning and Stock (36)

| T°K. | Pressure in mm. Hg. | $(\Delta H_s)_{t.p.}$ |
|---|---|---|
| 76.89 | 8.72 | 2303 |
| 79.75 | 15.00 | 2313 |
| 80.21 | 16.00 | 2340 |
| 81.74 | 21.80 | 2283 |
| 83.82 | 30.78 | 2297 |
| 85.42 | 40.26 | 2271 |
| 86.43 | 46.70 | 2303 |
| 87.25 | 53.35 | 2266 |

We substitute the average value of $(\Delta H_s)_{t.p.}$, 2297 ± 18 calories per gram-mole, in the equation which we derived from equation (15) and obtain for the vapor pressure of methane from the triple point at 90.66°K. to 21.35°K.

$$\log p(mm) = 2.0216 - \frac{478.51}{T} + 4 \log T - 0.2086T^{0.5624} \qquad (48)$$

On comparison of the vapor pressures calculated by equation (48) with the National Bureau of Standards equation (10) adjusted by Armstrong, Brickwedde, and Scott (11), we find the temperature change required to obtain equal vapor pressures is less than ± 0.1°K. The vapor pressure equation developed by Armstrong, Brickwedde, and Scott (11) for the range 54°K. to 90.66°K. checks to within less than ± 0.1°K. down to 70°K. and

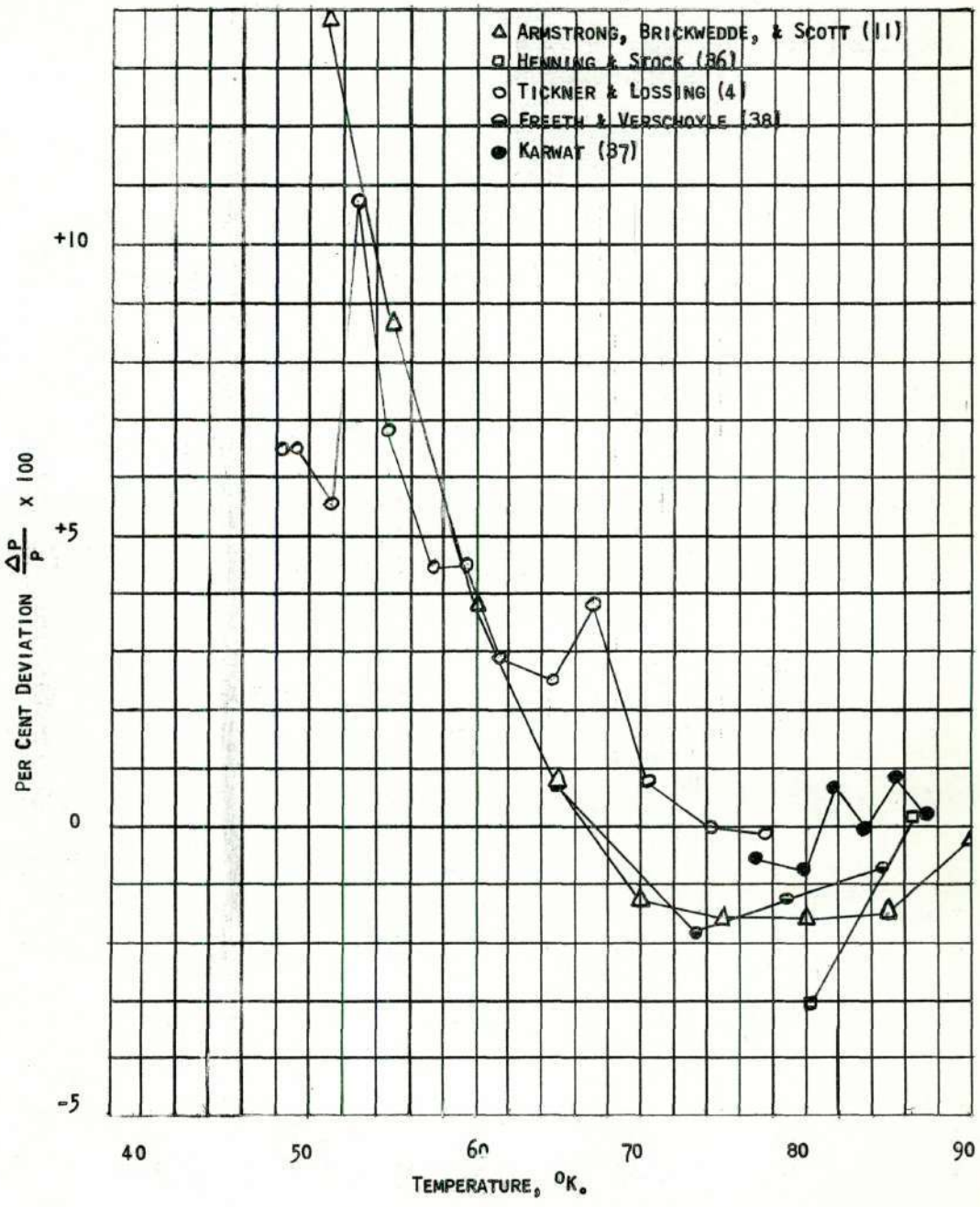


FIGURE 5. PER CENT DEVIATION OF OBSERVED VAPOR PRESSURE OF METHANE FROM THAT CALCULATED USING EQUATION (48).

rises to slightly less than +.43°K. at 54°K. The equation developed by Armstrong, Brickwedde, and Scott (11) deviates no more than 0.1 mm. Hg. from the equation previously developed by the National Bureau of Standards (10) which Armstrong, Brickwedde, and Scott corrected. They plotted the deviations of their observed vapor pressures from the vapor pressure equation which they developed. The deviations in mm. of Hg. below 60°K. shown by them are equal to or greater than the vapor pressure of methane in this region because the vapor pressure is less than the accuracy of 0.1 mm. Hg. to which Armstrong, Brickwedde, and Scott could read the vapor pressure. Armstrong, Brickwedde, and Scott (11) calculated and tabulated the vapor pressures of methane at 1° intervals from 90°K. to 51°K. using equation (45).

The experimental data of Karwat (37) and Henning and Stock (36) require a temperature change of less than ± 0.08°K. with the exception of one measurement of Henning and Stock at 80.21°K. which requires a -0.14°K. change. The experimental data of Freeth and Verschoyle (38) require a temperature change of less than -0.05°K. The data of Tickner and Lossing (4) check to a temperature change of less than + 0.18°K. with the exception of 2 points which require +0.32°K. which is within the stated accuracy of their measurements.

The calculations of Liang (5) show that the effect of thermal transpiration must be considered for methane. There is some variation in the experimental data below 55°K. By basing our equation on experimental vapor pressure data above 75°K. we eliminate the effect of thermal transpiration on our data. Accordingly, we would expect vapor pressure data calculated by our equation to vary consistently lower than experimental values below 55°K. as it does.

The deviation of the available vapor pressure data on methane from the vapor pressure calculated from equation (48) is plotted as a function of the absolute temperature in Figure 5. The deviation, $P_{observed}-P_{calculated}/P_{calculated}$, is expressed as per cent.

It is concluded that equation (48) yields results for the vapor pressure of solid methane which are reliable to about $\pm$ 0.1°K. This corresponds to $\pm$ 0.03 mm. of mercury at 70°K. Failure to take into account the non-classical rotational contribution to the zero pressure heat capacity in our calculation introduces a maximum error of approximately 30 per cent in the vapor pressure equation at the lowest temperatures. This error is no greater than that resulting from an error of $\pm$ 0.1°K. in the temperature.

The equation was based on heat capacity data down to 21.35°K. as previously stated; therefore, the solid transition point at 20.44°K. and the boiling point of hydrogen at 20.4°K. were not reached. An extrapolation of equation (48) an additional 1°K. should give accuracy equal to that at 21.35°K.

The vapor pressure of solid methane calculated from equation (48) is tabulated in Table 9. A plot of log p(mm) as a function of the reciprocal of the absolute temperature, 1/T°K., is shown in Figure 2. The triple point and solid transition point of methane and the boiling point of hydrogen are marked on the plot by vertical lines and the value of the absolute temperature in °K.

Table 9. Vapor Pressure of Solid Methane

| Temperature, °K | Pressure in mm Hg. |
|---|---|
| 90.66 (triple point) | 87.5 |
| 90 | 79.8 |
| 85 | 37.4 |
| 80 | 15.8 |
| 75 | 6.0 |
| 70 | 2.0 |
| 65 | $5.4 \times 10^{-1}$ |
| 60 | $1.2 \times 10^{-1}$ |
| 55 | $2.0 \times 10^{-2}$ |
| 50 | $2.3 \times 10^{-3}$ |
| 45 | $1.7 \times 10^{-4}$ |
| 40 | $6.2 \times 10^{-6}$ |
| 35 | $1 \times 10^{-7}$ |
| 30 | $4 \times 10^{-10}$ |
| 25 | $2 \times 10^{-13}$ |
| 20.44 (transition) | --- |
| 20.4 | $5 \times 10^{-18}$ |

Vapor Pressure of Oxygen from Its Triple Point to the Boiling Point of Hydrogen at 20.4°K.

Review of the Literature.--The National Bureau of Standards (45) has made a critical compilation of the measured experimental vapor pressure down to the triple point of oxygen. The only available data for the vapor pressure of solid oxygen are the measurements of Aoyama and Kanda (2) which do not appear to be very reliable (3) and consequently were not included in the National Bureau of Standards tabulation. The triple point of oxygen was established as 54.363°K. with a vapor pressure at the triple point of 1.14 mm. Hg. in the National Bureau of Standards compilation (45).

In the absence of accurate vapor pressure measurements below the triple point, we must rely on the experimental data at the triple point and above to evaluate the heat of sublimation, $(\Delta H_s)_{t.p.}$, at the triple point.

The available data on the two solid transition points have been compiled by Hoge (3) who also measured the transitions and found them to be 43.8°K. and 23.9°K. The heats of transition and fusion were measured by Clusius (27), Eucken (26), and Giauque and Johnston (46). The values obtained by Giauque and Johnston (46) will be used in our calculations. The heat of vaporization at the normal boiling point has been measured by Frank and Clusius (47) and Giauque and Johnston (46) who also compiled data from the literature for comparison. We will use the average of the heat of vaporization obtained by Dana (48), Giauque and Johnston (46), and Frank and Clusius (27).

The zero pressure heat capacity has been compiled by the National Bureau of Standards (45) and is essentially constant over the temperature range being considered.

The heat capacity of liquid and solid oxygen from the boiling point at 90.19°K. to below 20.4°K. have been measured by Giauque and Johnston (46), and Clusius (27), and Eucken (26). Giauque and Johnston (46) found that their data differ considerably from the data of Eucken (26) at the lower temperatures. The difference is attributed to Eucken's temperature scale between the liquid hydrogen and liquid air regions. There is good agreement over the entire range between the data of Giauque and Johnston (46), on which we will base our calculation, and Clusius (27).

The heat capacity of liquid oxygen from the triple point at 54.363°K. to the boiling point at 90.19°K. is represented by the equation

$$C_p = 11.78 + 0.0147T \qquad (49)$$

For solid oxygen from the triple point at 54.363°K. to the first solid transition point at 43.8°K. the heat capacity data is represented by

$$C_p = 11.02 \tag{50}$$

Below the first solid transition point at 43.8°K. to the second transition point at 23.9°K. the heat capacity data are represented by the equation

$$C_p = -2.58 + 0.3115T \tag{51}$$

and from the second solid transition to 20.4°K. by the equation

$$C_p = -6.35 + 0.4813T \tag{52}$$

The data were fitted to the equation by the method of averages discussed by Lipka (21). Equation (49) reproduces the data of Giauque and Johnston (46) to within an average of ± 0.5 per cent. Equation (51) reproduces the data of Giauque and Johnston (46) and Clusius (27) to within an average of ± 1.5 per cent. Equation (52) reproduces the data of both to within an average of ± 1.75 per cent.

The second virial coefficients of van Itterbeek and van Paemel (49) were used to obtain the correction for gas imperfection at the boiling point of oxygen.

The data discussed in this section are tabulated in the appendix.

The Vapor Pressure Equation for Solid Oxygen.--The calculations on oxygen are included for illustrative purposes in the appendix in the sample calculations. We note that sufficient experimental data are available to

to evaluate the heat of sublimation at the triple point by the procedure outlined in Chapter III for vapor pressure equations of solids based on experimental data at and above the triple point. We substitute the proper values in equation (25) and equation (33), and obtain the heat of vaporization of liquid oxygen at the triple point to which we add the heat of fusion and obtain the heat of sublimation at the triple point, 1947 calories per gram-mole.

Table 10. Oxygen Calorimetric Data Used

| Temperature, °K | Pressure mm.Hg. | H, Calories gm.-mole | Process |
|---|---|---|---|
| 90.19 (boiling point) | 760 | 1630 | vaporization |
| 54.363 (triple point) | 1.14 | 1841 | vaporization (calc.) |
| | | 106.3 | fusion |
| | | 1947 | sublimation (calc.) |
| 43.8 (transition) | --- | 177.6 | transition |
| 23.9 (transition) | --- | 22.42 | transition |

The zero pressure heat capacity is treated as constant and the heat capacities of the three solid forms of oxygen are linear. The vapor pressure equation for solid oxygen from the triple point at 54.363°K. to the transition point will have the form of equation (18) as will the vapor pressure equations for the other two forms of solid oxygen after substituting the proper values in equation (21) and equation (22) and performing the indicated operations.

We substitute the value of $(\Delta H_s)_{t.p.}$ in equation (18) and obtain the vapor pressure equation for solid oxygen from the triple point at 54.363°K. to the first transition point at 43.8°K.

$$\log p(mm) = 12.3161 - \frac{473.71}{T} \qquad (53)$$

$$- 2.0431 \log T$$

We substitute the proper values in equation (21) and (22) and obtain the vapor pressure equation for solid oxygen from the first transition point at 43.8°K. to the second transition point at 23.9°K.

$$\log p(mm) = 1.9703 - \frac{447.50}{T} \qquad (54)$$

$$+ 4.8018 \log T - 0.03398T$$

In the same manner, we obtain the vapor pressure equation for solid oxygen from the second transition point at 23.9°K. to the boiling point of hydrogen at 20.4°K.

$$\log p(mm) = - 0.3882 - \frac{443.35}{T} \qquad (55)$$

$$+ 6.7095 \log T - 0.05258T$$

We compare the vapor pressure calculated by equation (53) with the three values of Hoge (3) which he measured but considered were not as reliable as his other measurements at the triple point and find his results on all but the lowest measurement agree with our equation to within ± 0.1°K. The data of Aoyama and Kanda is not consistent with our equation, just as we expected.

The deviation of the observed vapor pressure of oxygen from the vapor pressure calculated from equations (53), (54), and (55) is plotted as a function of the absolute temperature in Figure 6. The deviation, $P_{observed}-P_{calculated}/P_{calculated}$, is expressed as per cent.

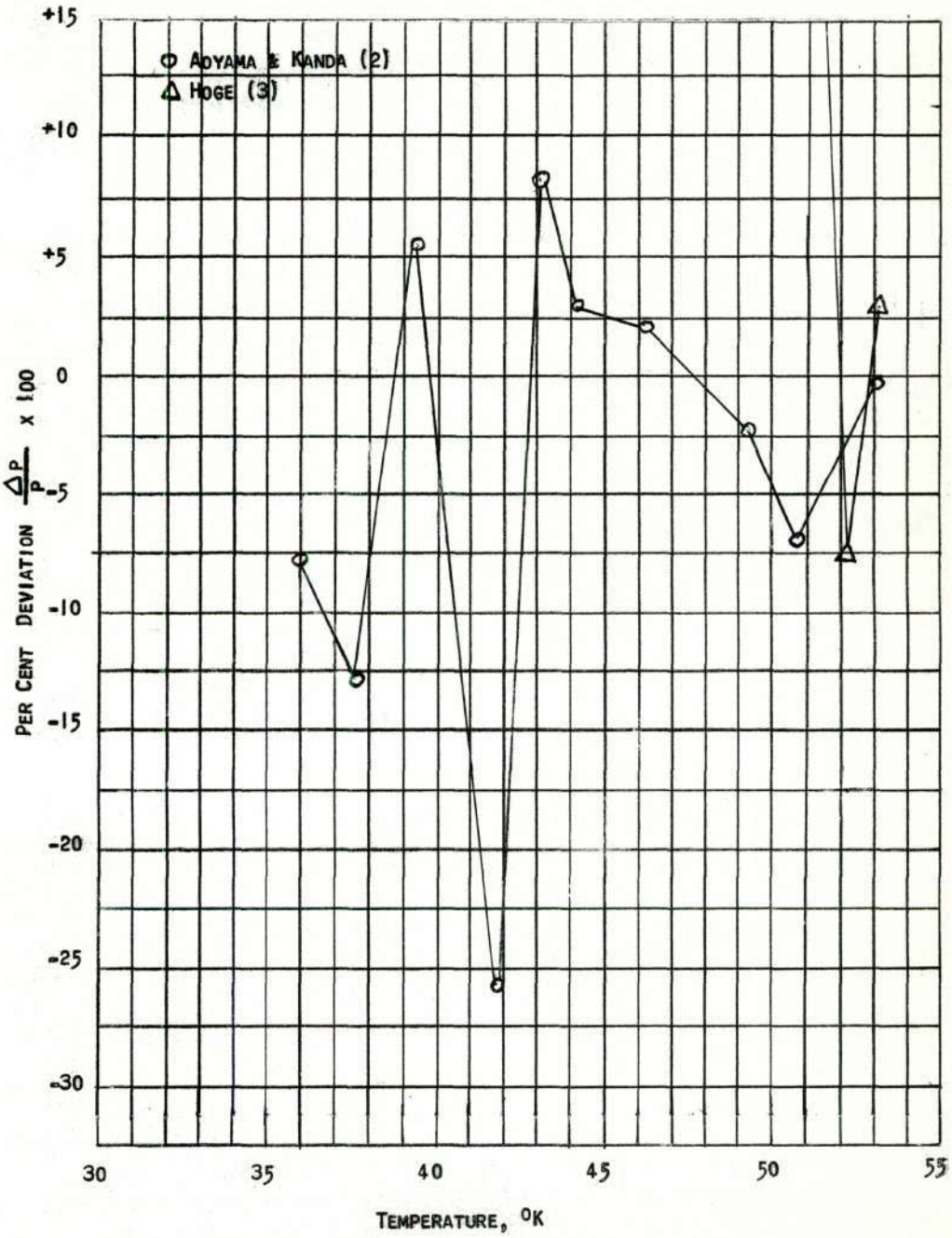


FIGURE 6. PER CENT DEVIATION OF OBSERVED VAPOR PRESSURE OF OXYGEN FROM THAT CALCULATED USING EQUATIONS (53) AND (54).

The vapor pressure data as calculated by equations (53), (54), and (55) are uncertain by no more than the previous vapor pressure equations of the other substances; however, the data necessary for testing this equation in the region below the triple point are very limited. The agreement of the two values for the vapor pressure obtained by Hoge (3) with equation (53) indicates consistency to at least $\pm$ 0.1°K. which corresponds to $\pm$ 0.01 mm. of Hg. at 50°K.

The vapor pressure of solid oxygen calculated from equations (53), (54), and (55) is tabulated in Table 11. A plot of log p(mm) as a function of the reciprocal of the absolute temperature, 1/T°K., is shown in Figure 2. The triple point and transition points of solid oxygen and the normal boiling point of hydrogen are marked on the plot with vertical lines and the absolute temperature in °K.

Table 11. Vapor Pressure of Solid Oxygen

| Temperature, °K. | Pressure, mm. Hg. |
|---|---|
| 54.363 (triple point) | 1.14 |
| 50.00 | 0.24 |
| 45.00 | $2.6 \times 10^{-2}$ |
| 43.80 (transition) | $1.4 \times 10^{-2}$ |
| 40.00 | $1.3 \times 10^{-3}$ |
| 35.00 | $2.6 \times 10^{-5}$ |
| 30.00 | $1.3 \times 10^{-7}$ |
| 25.00 | $9 \times 10^{-11}$ |
| 23.90 (transition) | $1 \times 10^{-11}$ |
| 20.40 | $4 \times 10^{-15}$ |

# CHAPTER V

## DISCUSSION OF RESULTS

Vapor Pressure Equations of the Gases.--Vapor pressure equations for the solid phases of argon, carbon monoxide, methane, nitrogen, and oxygen have been developed from their triple points to the boiling point of hydrogen at 20.4°K. The equations are based on fundamental thermodynamic relationships and the most reliable data from the literature. Great reliance was placed on the compilation of the National Bureau of Standards (9).

The vapor pressures calculated from the equations developed have been compared with experimental vapor pressure data from the literature and good agreement was obtained. In general, the variations can be attributed to differences in the thermodynamic temperature scales used. The change in temperature required to make the vapor pressures calculated from our equations equal to the experimental vapor pressures ranged from less than $\pm$ 0.1°K. to $\pm$0.2°K. with the major deviations occurring at the lower temperatures farther from the triple points. Figures 1, 3, 4, 5, and 6 are plots of the deviation, $P_{observed}-P_{calculated}/P_{calculated}$ expressed as per cent, plotted as a function of the absolute temperature.

Our equations based on more reliable data at or near the triple point eliminate the thermal transpiration effects at the lower temperatures. This effect is most pronounced in the case of methane because the experimental data go to the lowest pressures.

Tables of the vapor pressures of the solids calculated at five degree intervals, including the triple and transition points down to the boiling point of hydrogen at 20.4°K., have been included for convenience in obtaining vapor pressures. In addition, plots of the log p(mm) as a function of the reciprocal of the absolute temperature, $1/T^{\circ}K.$, are included in Chapter IV for obtaining vapor pressures.

Sample calculations on argon and oxygen are presented in the appendix to show the procedure for calculating the vapor pressures of solids with no experimental vapor pressure data available below the triple point, with no transitions, and with transitions below the triple point.

Value of the Equations.--A method for developing special vapor pressure equations for solids based on the general equation of Fowler (12) has been developed and outlined in Chapters II and III. The method has been used to develop the vapor pressure equations of argon, carbon monoxide, methane, nitrogen, and oxygen which have been compared with experimental values to test the validity of our method and to obtain vapor pressure equations for the substances in an area where vapor pressure data is lacking and measurement is time consuming, expensive, and subject to many sources of error.

Equations developed in this manner should give greater reliability than extrapolated data and the method should be applicable to cases other than gases at low temperatures as for example metals and salts at higher temperatures.

These equations have certain limitations arising from the uncertainties in the heat of sublimation, the failure to include the difference between the enthalpy of the saturated vapor and the ideal gas, and the uncertainties in the thermal data for the condensed phases. It is believed

that these uncertainties may lead to errors of as much as a factor of two in the computed vapor pressures near 20°K. This uncertainty is equivalent to approximately ± 0.2°K.

# CHAPTER VI

## CONCLUSIONS

Concerning the Vapor Pressure Equations of the Gases.--The vapor pressure equations for the solid phases of argon, carbon monoxide, methane, nitrogen, and oxygen developed from their triple points to the boiling point of hydrogen at 20.4°K. compare well with experimental values of vapor pressure obtained by reliable experimenters as reported in the literature. The change in temperature required to make the vapor pressures calculated by our equations equal to the experimental vapor pressures is about $\pm$ 0.1°K.

The thermal transpiration effect has been eliminated in our vapor pressure equations by using experimental vapor pressure data in the temperature regions where the effect is negligible. At lower temperatures the thermal transpiration effect is not, therefore, present in theoretically derived equations, but must be considered in experimental vapor pressure determinations.

Since our equations are based on fundamental thermodynamic relationships applicable over the temperature range considered and reliable experimental data in regions near the triple points where the accuracy is high, our vapor pressure equations for the individual substances yield values for the vapor pressure of the solids with greater reliability than could be obtained on extrapolation of experimental vapor pressure data to lower temperatures.

Concerning the Method of Calculation.--The method of calculation outlined in Chapter II and Chapter III based on fundamental thermodynamic relation-

ships and reliable experimental data can be used to develop vapor pressure equations of other solid substances such as metals and salts at higher temperatures.

# APPENDIX

VAPOR PRESSURE DATA FROM THE LITERATURE

Argon

Table 12. Vapor Pressure of Solid Argon

Data of National Bureau of Standards (13)

| Temperature, °K. | Pressure, mm. Hg. |
|---|---|
| 83.78 (triple point) | 516.8 |
| 87.29 (boiling point) | 760.0 |
| 65 | 21 |
| 70 | 58 |
| 75 | 141 |
| 80 | 306 |

Table 13. Vapor Pressure of Solid Argon

Data of Clark, Din, Robb, Michels, Wassenaar, and Zwietering (19)

| Temperature, °K. | Pressure, mm. Hg. |
|---|---|
| 70 | 57.7 |
| 72 | 83.5 |
| 74 | 118.5 |
| 76 | 165.1 |
| 78 | 226.1 |
| 80 | 304.8 |
| 82 | 405.0 |
| 83.78 (triple point) | 515.7 |

Table 14. Vapor Pressure of Solid Argon

Data of Crommelin (15)

| Temperature, °C | Pressure, International cm. of Hg. |
|---|---|
| -189.30 (triple point) | 51.565 |
| -191.36 | 39.429 |
| -194.58 | 25.101 |
| -197.62 | 16.348 |
| -206.04 | 6.717 |

Table 15. Vapor Pressure of Solid Argon

Data of Crommelin (16)

| Temperature, °C | Pressure, International cm. of Hg. |
|---|---|
| -189.64 | 49.78 |
| -191.31 | 39.30 |
| -195.60 | 20.88 |
| -197.25 | 16.35 |
| -200.97 | 8.456 |
| -202.21 | 6.783 |
| -203.78 | 5.119 |
| -205.32 | 3.830 |

Table 16. Vapor Pressure of Solid Argon

Data of Born (8)
Table 2

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 65.49 | 21.97 |
| 66.16 | 25.36 |
| 69.43 | 47.97 |
| 70.49 | 59.26 |
| 71.95 | 77.47 |
| 73.93 | 111.78 |
| 75.50 | 146.0 |
| 76.69 | 176.9 |
| 77.48 | 200.6 |
| 79.06 | 255.6 |
| 80.60 | 321.2 |
| 81.42 | 360.5 |
| 82.75 | 435.9 |
| 83.21 | 464.3 |
| 83.93 | 512.17 |

Carbon Monoxide

Table 17. Vapor Pressure of Solid Carbon Monoxide

Data of Clayton and Giauque (7)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 62.22 | 32.75 |
| 63.30 | 42.30 |
| 64.31 | 52.83 |
| 65.28 | 65.46 |
| 66.12 | 77.69 |
| 67.02 | 93.25 |

Table 18. Vapor Pressure of Solid Carbon Monoxide

Data of National Bureau of Standards (22)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 55 | 4.21 |
| 60 | 18.56 |
| 65 | 61.2 |
| 68.09 (triple point) | 115.3 |

Table 19. Vapor Pressure of Solid Carbon Monoxide

Data of Verschoyle (6)

| Temperature, °K. | Pressure, in mm. Hg. |
|---|---|
| 68.13 | 114.86 |
| 65.73 | 70.45 |
| 62.34 | 32.94 |
| 60.38 | 19.87 |
| 57.45 | 8.86 |
| 54.28 | 3.26 |

Table 20. Vapor Pressure of Solid Carbon Monoxide

Data of Crommelin, Bijleveld, and Brown (23)

| Temperature, °C | Pressure, in mm. of Hg. |
|---|---|
| -205.02 | 114.90 |
| -205.19 | 110.70 |
| -205.95 | 97.78 |
| -206.46 | 81.04 |
| -207.42 | 70.56 |
| -208.13 | 60.75 |
| -210.41 | 36.48 |
| -216.23 | 7.215 |

Table 21. Vapor Pressure of Solid Carbon Monoxide

Data of Clusius and Teske (24)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 60.36 | 20.41 |
| 60.616 | 20.83 |
| 61.455 | 24.59 |
| 61.985 | 30.83 |
| 63.974 | 44.65 |
| 64.348 | 55.19 |
| 64.892 | 60.99 |
| 65.967 | 77.55 |
| 66.201 | 79.65 |
| 67.171 | 98.88 |
| 67.373 | 99.63 |
| 68.213 | 117.08 |

Nitrogen

Table 22. Vapor Pressure of Solid Nitrogen

Data of the National Bureau of Standards (30)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 63.156 (triple point) | 94.0 |
| 62 | 73.6 |
| 60 | 47.2 |
| 58 | 29.4 |
| 56 | 17.6 |
| 54 | 10.2 |
| 52 | 5.7 |

Table 22. Vapor Pressure of Solid Nitrogen

Data of Dokoupil, Van Soest, and Swenker (1)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 60.5 | 54.8 |
| 47.5 | 1.20 |
| 46.9 | 0.83 |
| 46.2 | 0.73 |
| 45.4 | 0.47 |
| 42.1 | 0.16 |

Table 24. Vapor Pressure of Solid Nitrogen

Data of Clayton and Giauque (32)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 54.783 | 12.73 |
| 55.875 | 17.10 |
| 56.930 | 22.44 |
| 57.850 | 28.40 |
| 58.741 | 35.26 |
| 59.550 | 42.85 |
| 60.670 | 55.26 |
| 61.700 | 69.58 |
| 63.136 (triple point) | 94.01 |

Table 25. Vapor Pressure of Solid Nitrogen

Data of Henning (34)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 62.740 | 85.77 |
| 61.880 | 70.27 |
| 61.723 | 69.26 |
| 60.883 | 58.36 |
| 62.232 | 77.44 |

Table 26. Vapor Pressure of Solid Nitrogen

Data of Keesom and Bijl (31)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 63.102 | 92.97 |
| 60.783 | 56.43 |
| 58.106 | 22.97 |
| 55.821 | 16.80 |
| 53.264 | 8.225 |

Table 27. Vapor Pressure of Solid Nitrogen

Data of Von Siemens (33)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 63.17 | 93.5 |
| 62.79 | 86.1 |
| 61.95 | 71.9 |
| 60.77 | 55.3 |
| 59.95 | 45.8 |
| 58.71 | 34.1 |
| 57.70 | 26.4 |
| 56.97 | 21.8 |

Table 28. Vapor Pressure of Solid Nitrogen

Data of Aoyama and Kanda (2)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 62.54 | 76.2 |
| 58.79 | 38.2 |
| 56.80 | 16.6 |
| 49.61 | 2.62 |
| 45.90 | 0.577 |
| 43.00 | 0.144 |
| 42.11 | 0.105 |
| 39.81 | 0.035 |
| 39.63 | 0.035 |
| 37.41 | 0.0088 |
| 36.54 | 0.0048 |
| 35.40 | - |
| 34.69 | 0.0015 |
| 33.71 | 0.00063 |
| 30.80 | 0.00005 |

Methane

Table 29. Vapor Pressure of Solid Methane

Data of National Bureau of Standards (10)
Corrected by Armstrong, Brickwedde, and Scott (11)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 90.66 (triple point) | 87.50 |
| 90.00 | 79.56 |
| 88.00 | 59.11 |
| 86.00 | 43.33 |
| 84.00 | 31.31 |
| 82.00 | 22.27 |
| 80.00 | 15.58 |
| 77.65 | 10.01 |

Corrected NBS Equation for Vapor Pressure of Solid Methane:

$$\log p(\text{mm}) = 7.6950 - 532.20/(T+1.842) \qquad (50)$$

Equation of Armstrong, Brickwedde, and Scott (11) for vapor pressure of solid methane over range 54°K. to 90.66°K.

$$\log_{10}p(mm) = 6.7838 - 477.46/T + 0.00469T \qquad (56)$$

Table 30. Vapor Pressure of Solid Methane

Data of Tickner and Lossing (4)

| Temperature, °K | Pressure, mm. of Hg. |
|---|---|
| 77.66 | 10 |
| 74.16 | 5 |
| 70.06 | 2 |
| 67.16 | 1 |
| 64.66 | 0.5 |
| 61.56 | 0.2 |
| 59.36 | 0.1 |
| 57.36 | 0.05 |
| 54.86 | 0.02 |
| 53.06 | 0.01 |
| 51.56 | 0.005 |
| 49.56 | 0.002 |
| 48.16 | 0.001 |

Table 31. Vapor Pressure of Solid Methane

Data of Henning and Stock (36)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 80.21 | 16.00 |
| 86.43 | 46.70 |

Table 32. Vapor Pressure of Solid Methane

Data of Karwat (37)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 76.89 | 8.72 |
| 79.75 | 15.00 |
| 81.74 | 21.80 |
| 83.82 | 30.78 |
| 85.42 | 40.26 |
| 87.25 | 53.35 |

Table 33. Vapor Pressure of Solid Methane

Data of Freeth and Verschoyle (38)

| Temperature, °C. | Pressure, mm. of Hg. |
|---|---|
| -182.47 | 87.67 |
| -188.49 | 35.13 |
| -194.16 | 13.04 |
| -199.70 | 4.24 |
| -208.32 | 0.506 |

Oxygen

Table 34. Vapor Pressure of Solid Oxygen

Data of Hoge (3)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 51.296 | 0.47 |
| 52.176 | 0.53 |
| 53.082 | 0.76 |
| 54.363 (triple point) | 1.14 |

Table 35. Vapor Pressure of Solid Oxygen

Data of Aoyama and Kanda (2)

| Temperature, °K. | Pressure, mm. of Hg. |
|---|---|
| 54.36 | 1.20 |
| 53.02 | 0.708 |
| 50.74 | 0.291 |
| 49.38 | 0.178 |
| 46.09 | 0.045 |
| 44.11 | 0.022 |
| 43.5 | - |
| 43.09 | 0.0101 |
| 41.91 | 0.0034 |
| 41.58 | 0.0048 |
| 39.41 | 0.00092 |
| 37.62 | 0.00020 |
| 36.00 | 0.00006 |

## TRIPLE POINT DATA FROM THE LITERATURE

Table 36. Triple Point Data Used

| Substance | Triple Point, °K | Pressure, mm. of Hg. | Reference |
|---|---|---|---|
| A | 83.78 | 516.8 | NBS (13) |
| CO | 68.09 | 115.3 | NBS (22) |
| $CH_4$ | 90.66 | 87.5 | Armstrong, Brickwedde, and Scott (11) |
| $N_2$ | 63.156 | 94.0 | NBS (30) |
| $O_2$ | 54.363 | 1.14 | Hoge (3) |

## TRANSITION POINT DATA FROM THE LITERATURE

Table 37. Transition Point Data Used

| Substance | Transition Point °K | Pressure, mm. Hg. | Reference |
|---|---|---|---|
| CO | 61.57 | 28.1 | NBS (22) |
| $CH_4$ | 20.44 | - | Clusius (27) |
| $N_2$ | 35.62 | - | NBS (30) |
| $O_2$ | 43.8 | - | Hoge (3) |
| $O_2$ | 23.9 | - | Hoge (3) |

## HEAT OF TRANSITION DATA FROM THE LITERATURE

Table 38. Heat of Transition Data Used

| Substance | Transition Point, °K. | Heat of Transition Calories/gm-mole | Reference |
|---|---|---|---|
| CO | 61.57 | 151.8 | Clayton and Giauque (7) |
| $N_2$ | 35.62 | 54.71 | Clayton and Giauque (32) |
| $O_2$ | 43.8 | 177.6 | Giauque and Johnston (46) |
| $O_2$ | 23.9 | 22.42 | Giauque and Johnston (46) |

## HEATS OF VAPORIZATION AND FUSION OF OXYGEN

Table 39. Heats of Vaporization and Fusion of Oxygen Used

| Substance | Normal Boiling Point, °K. | Heat of Vaporization Calories gm.-mole | Heat of Fusion Calories gm.-mole | Reference |
|---|---|---|---|---|
| $O_2$ | 90.19 | - | - | NBS (45) |
| $O_2$ | - | 1628.1 | - | Giauque and Johnston (46) |
| $O_2$ | - | 1630.7 | - | Frank and Clusius (47) |
| $O_2$ | - | 1631.7 | - | Dana (48) |
| $O_2$ | - | - | 106.3 | Giauque and Johnston (46) |

## ZERO PRESSURE HEAT CAPACITIES

Table 40. Zero Pressure Heat Capacity of Oxygen

Data of National Bureau of Standards (45)

| Temperature, °K. | $C_p^o/R$ |
|---|---|
| 10 | 3.5423 |
| 20 | 3.5145 |
| 30 | 3.5077 |
| 40 | 3.5044 |
| 50 | 3.5029 |
| 60 | 3.5023 |
| 70 | 3.5019 |
| 80 | 3.5016 |
| 90 | 3.5015 |
| 100 | 3.5014 |

To convert to calories/gm.-mole °K. multiply by 1.98719.

Table 41. Zero Pressure Heat Capacity of Carbon Monoxide

Data of National Bureau of Standards (22)

| Temperature, °K. | $C_p^o/R$ |
|---|---|
| 60 | 3.500 |
| 70 | 3.500 |
| 80 | 3.500 |
| 90 | 3.500 |
| 100 | 3.500 |

To convert to calories/gm.-mole - °K. multiply by 1.98719.

Table 42. Zero Pressure Heat Capacity of Nitrogen

Data of National Bureau of Standards (30)

| Temperature, °K. | $C_p^o/R$ |
|---|---|
| 10 | 3.5019 |
| 20 | 3.5006 |
| 30 | 3.5004 |
| 40 | 3.5003 |
| 50 | 3.5003 |
| 60 | 3.5003 |
| 70 | 3.5003 |
| 80 | 3.5004 |

To convert to calories/gm.-mole - °K. multiply by 1.98719.

Table 43. Rotational Contribution to Heat Capacity of Methane

Data of MacDougall (44)

| Temperature, °K | Equilibrium Cr/R | 5/16 Quintet<br>9/16 Triplet Cr/R<br>2/16 Singlet |
|---|---|---|
| 3.84 | 0.499 | 0.020 |
| 7.68 | 0.941 | 0.290 |
| 12.80 | 1.347 | 0.642 |
| 19.20 | 1.733 | 1.198 |
| 25.60 | 1.838 | 1.592 |
| 30.72 | 1.798 | 1.696 |
| 38.40 | 1.688 | 1.667 |
| 43.89 | 1.621 | 1.615 |
| 51.20 | 1.563 | 1.561 |
| 61.44 | 1.527 | 1.527 |
| 76.80 | 1.504 | 1.504 |
| 153.60 | 1.500 | 1.500 |

VIRIAL COEFFICIENTS FROM THE LITERATURE

Table 44. Second Virial Coefficient of Oxygen

Data of van Itterbeek and van Paemel (49)

| Temperature, °K. | $-10^3$ B |
|---|---|
| 200 | 2.12 |
| 150 | 3.93 |
| 125 | 5.64 |
| 120 | 6.07 |
| 110 | 7.03 |
| 100 | 8.10 |
| 90 | 9.30 |
| 80 | 10.96 |
| 75 | 12.43 |

# HEAT CAPACITY OF LIQUIDS

Table 45. Heat Capacity of Liquid Oxygen

Data of Giauque and Johnston (46)

| Temperature, °K. | Cp Calories/gm-mole-°K. |
|---|---|
| 56.95 | 12.76 |
| 57.95 | 12.72 |
| 60.97 | 12.71 |
| 61.48 | 12.71 |
| 65.57 | 12.71 |
| 65.92 | 12.71 |
| 68.77 | 12.73 |
| 69.12 | 12.75 |
| 70.67 | 12.77 |
| 71.38 | 12.78 |
| 73.31 | 12.81 |
| 74.95 | 12.85 |
| 75.86 | 12.80 |
| 77.58 | 12.84 |
| 78.68 | 12.83 |
| 81.13 | 12.88 |
| 82.31 | 12.86 |
| 82.96 | 12.88 |
| 84.79 | 12.93 |
| 86.43 | 12.91 |
| 86.61 | 12.95 |
| 86.97 | 12.92 |
| 87.32 | 12.91 |
| 90.33 | 12.99 |

HEAT CAPACITY OF SOLIDS

Table 46. Heat Capacity of Solid Oxygen

Data of Giauque and Johnston (46)

| Temperature, °K. | Cp, Calories/gm.-mole-K. |
|---|---|
| 20.33 | 3.52 |
| 20.85 | 3.60 |
| 21.84 | 4.20 |
| 22.24 | 4.27 |
| 22.24 | 4.40 |
| Transition at 23.66°K. | |
| 25.02 | 5.42 |
| 25.61 | 5.57 |
| 25.61 | 5.47 |
| 26.75 | 5.75 |
| 28.00 | 6.05 |
| 28.08 | 6.42 |
| 29.88 | 6.61 |
| 30.63 | 6.94 |
| 31.08 | 6.93 |
| 33.05 | 7.52 |
| 33.33 | 7.73 |
| 34.41 | 8.08 |
| 35.57 | 8.26 |
| 35.77 | 8.49 |
| 37.59 | 9.08 |
| 37.85 | 9.12 |
| 38.47 | 9.80 |
| 39.99 | 9.80 |
| 40.18 | 9.92 |
| 40.67 | 10.16 |
| 42.21 | 10.73 |
| Transition at 43.76°K. | |
| 45.90 | 11.02 |
| 47.76 | 11.07 |
| 48.11 | 11.01 |
| 48.97 | 10.99 |
| 50.55 | 11.01 |
| 51.68 | 11.03 |
| 52.12 | 11.06 |
| Triple Point at 54.39°K. | |

Table 47. Heat Capacity of Solid Carbon Monoxide

Data of Clayton and Giaque (7)

| Temperature, °K | Cp, calories/gm-mole-°K. |
|---|---|
| 19.37 | 3.268 |
| 21.93 | 3.976 |
| 24.31 | 4.573 |
| 26.64 | 5.114 |
| 29.01 | 5.681 |
| 31.56 | 6.272 |
| 39.85 | 8.111 |
| 44.21 | 9.055 |
| 44.71 | 9.089 |
| 47.90 | 9.888 |
| 48.34 | 9.937 |
| 52.34 | 11.01 |
| 55.07 | 11.73 |
| 56.82 | 12.71 |
| 59.04 | 13.61 |
| Transition at 61.55°K. | |
| 63.47 | 12.02 |
| 64.55 | 12.16 |
| 66.02 | 12.30 |
| Triple point at 68.09°K. | |

Table 48. Heat Capacity of Solid Argon

Data of Clusius and Frank (20)

| Temperature, °K. | Cp, Calories/gm-mole-°K. |
|---|---|
| 20.32 | 2.88 |
| 21.95 | 3.13 |
| 22.0 | 3.07 |
| 24.4 | 3.61 |
| 28.4 | 4.23 |
| 32.4 | 4.64 |
| 36.1 | 4.98 |
| 39.7 | 5.27 |
| 43.35 | 5.53 |
| 47.0 | 5.70 |
| 51.0 | 5.98 |
| 56.0 | 6.17 |
| 60.8 | 6.41 |
| 65.95 | 6.78 |
| 70.9 | 7.04 |
| 71.6 | 7.10 |
| 76.1 | 7.44 |
| 79.6 | 7.63 |
| 80.3 | 7.77 |
| Triple point at 83.85°K. | |

Table 49. Heat Capacity of Solid Nitrogen

Data of Clayton and Giauque (32)

| Temperature, °K. | Cp, Calories/gm-mole-°K. |
|---|---|
| 19.51 | 4.577 |
| 21.94 | 5.447 |
| 24.49 | 6.331 |
| 24.85 | 6.380 |
| 27.14 | 7.170 |
| 28.32 | 7.540 |
| 29.89 | 8.137 |
| 31.29 | 8.643 |
| 32.84 | 9.397 |
| 34.42 | 10.28 |
| 34.68 | 10.49 |
| 35.05 | 10.84 |
| 35.33 | 10.67 |
| Transition at 35.61°K. | |
| 39.13 | 8.948 |
| 43.27 | 9.325 |
| 48.07 | 9.752 |
| 51.88 | 10.09 |
| 53.55 | 10.26 |
| 55.88 | 10.44 |
| 57.99 | 10.65 |
| 61.40 | 11.09 |
| 61.41 | 11.07 |
| Triple point at 63.14°K. | |

Table 50. Heat Capacity of Solid Methane

Data of Frank and Clusius (39)

| Temperature, °K. | Cp, Calories/gm-mole-°K. |
|---|---|
| 19.17 | 6.152 |
| 19.47 | 7.324 |
| 19.78 | 10.65 |
| 19.94 | 10.91 |
| 20.12 | 17.20 |
| 20.18 | 20.7 |
| 20.27 | 35.7 |
| 20.27 | 45.3 |
| 20.32 | 47.6 |
| 20.34 | 71.6 |
| 20.37 | 69.3 |
| 20.40 | 42.5 |
| 20.44 | 27.4 |
| 20.53 | 10.31 |
| 21.06 | 4.504 |
| 21.35 | 4.325 |
| 22.48 | 4.641 |
| 23.13 | 4.782 |
| 24.65 | 4.912 |
| 25.52 | 5.193 |

Table 51. Heat Capacity of Solid Methane

Data of Clusius (27)

| Temperature, °K | Cp, Calories/gm-mole-°K. |
|---|---|
| 20.21 | 13.31 |
| 20.48 | 40.50 |
| 20.44 | 48.74 |
| Transition at 20.44°K. | |
| 20.86 | 12.07 |
| 20.94 | 9.978 |
| 22.80 | 4.618 |
| 24.90 | 4.932 |
| 26.70 | 5.273 |
| 28.5 | 5.535 |
| 30.7 | 5.831 |
| 35.2 | 6.392 |
| 37.6 | 6.695 |
| 40.0 | 6.932 |
| 42.3 | 7.238 |
| 44.4 | 7.363 |
| 46.7 | 7.553 |
| 49.7 | 7.830 |
| 52.5 | 8.058 |
| 55.7 | 8.254 |
| 58.3 | 8.471 |
| 61.4 | 8.673 |
| 65.1 | 8.814 |
| 67.2 | 8.951 |
| 68.6 | 9.032 |
| 70.7 | 9.176 |
| 71.9 | 9.252 |
| 75.0 | 9.382 |
| 75.6 | 9.500 |
| 79.4 | 9.660 |
| 79.5 | 9.715 |
| 83.0 | 9.967 |
| 83.7 | 10.02 |
| 87.0 | 10.12 |
| 87.2 | 10.19 |
| Triple Point at 90.6°K. | |

## SAMPLE CALCULATIONS

Vapor Pressure Equation of Solids with No Transitions.--The calculations made on argon which has no transitions below the triple point will be used to illustrate the method of calculating the vapor pressure equation of solids with no transitions.

We examine equation (15) from Chapter II

$$\ln p - \ln p_o = \int_{T_{t.p.}}^{T} \frac{(\Delta H_s)_{t.p.}}{RT^2}\, dT + \int_{T_{t.p.}}^{T} \frac{1}{RT^2} \left[ \int_{T_{t.p.}}^{T} (C_p^o - C_{p_{sol}})\, dT \right] dT \qquad (15)$$

and note that we know or can calculate from experimental values reported in the literature, $\ln p_o$, $T_{t.p.}$, $C_p^o$, and $C_{p_{sol}}$. Thus, in equation (15) we have two unknowns, $\ln p$ and $(\Delta H_s)_{t.p.}$.

The zero pressure heat capacity, $C_p^o$, is constant over the temperature range, since argon is a monatomic gas. $C_p^o/R$ is given as 2.500 where R is 1.98719 calories/gm.-mole-$^oK$. Therefore, $C_p^o$ is 4.9679 calories/gm.-mole-$^oK$.

The heat capacity of solid argon from Table 48 is represented by the equation

$$C_p = 2.86 + 0.0600T - 6.8 \times 10^5\, T^{-4.35} \qquad (34)$$

for the temperature range from the triple point to 20.4°K.

We obtain ln $p_o$ and $T_{t.p.}$ from Table 12 where $p_o$ is the vapor pressure of argon at the triple point, 83.78°K. The logarithm is equal to 2.7133 at 83.78°K.

Substituting the known values in equation (15) and integrating, we obtain the equation for the vapor pressure of solid argon in terms of the two unknowns, log p and $(\Delta H_s)_{t.p.}$

$$\log p(mm) = -\frac{0.21851\ (\Delta H_s)_{t.p.}}{T} \qquad (57)$$

$$+ 1.0608 \log T - 0.006555T$$

$$+ 1.02 \times 10^4\ T^{-4.35}\ ^{-7.429/T}$$

$$+ 0.0026081\ (\Delta H_s)_{t.p.} + 1.3111$$

Substituting the logarithm of experimental vapor pressure and corresponding temperatures at which the experimental vapor pressures were obtained as tabulated in Tables 13, 14, and 15 in equation (57), we calculated the values of the heat of sublimation at the triple point, $(\Delta H_s)_{t.p.}$. The heats of sublimation at the triple point obtained in this manner are tabulated in Tables 1 and 2. Several extreme deviations obviously in error are excluded from Table 1. The average value of $(\Delta H_s)_{t.p.}$, giving equal weight to the data of the two groups of experimenters, is 1846 $\pm$ 14 calories/gm.-mole. Substituting this value in equation (57) we obtain the vapor pressure for solid argon from the triple point at 83.78°K. to the boiling point of

hydrogen at 20.4°K.

$$\log p(\text{mm}) = 6.1255 - \frac{410.78}{T} + 1.0608 \log T \qquad (58)$$

$$- 0.006555T + 1.02 \times 10^{4}\, T^{-4.35}$$

The last term of equation (58), $1.02 \times 10^{4}\, T^{-4.35}$, is due to the slight deviation of the specific heat equation (34) from linearity. Above a temperature of 55°K. this last term has no effect on the calculated vapor pressure and, therefore, can be neglected completely. Below 55°K. the vapor pressure calculated from equation (58) neglecting this last term is 5.0 per cent greater at 20.4°K. than the value calculated using the last term. The +5.0 per cent increase in the calculated vapor pressure at 20.4°K. is well within the reliability of the equation in terms of a $\pm$ 0.1°K. change in temperature. We, therefore, dispense with the last term of equation (48) sacrificing little reliability in the calculated value of the vapor pressure. Equation (58) is thus reduced to equation (35) which is found in Chapter IV.

The effect of pressure on the enthalpy of argon is not taken into consideration in the development of equation (35). In the case of oxygen this effect is negligible because of the low vapor pressure at its triple point. The vapor pressure of argon near the triple point is quite high; however, second virial coefficient data on argon over the temperature range under consideration was not found in the literature to make the correction.

Vapor Pressure Equation of Solids With No Experimental Vapor Pressure Data Available Below the Triple Point.--The calculations on the vapor pressure of solid oxygen will be used to illustrate the method of developing vapor

pressure equations for solids in the absence of experimental vapor pressure data on the solid.

We calculate the heat of vaporization of oxygen at the triple point, $(\Delta H_s)_{t.p.}$, by substituting the correct experimental values in equation (25) combined with equation (38)

$$(\Delta H_v)_{t.p.} = (\Delta H_v)_{b.p.} + \int_{b.p.}^{t.p.} (C_p^o - C_{Sat.\ liq.})\ dT \qquad (59)$$

$$- \frac{1}{R}\frac{dB}{dT}(p) + \frac{2B}{RT}$$

The zero pressure heat capacity, $C_p^o$, of oxygen is taken from Table 40 using the mean value of 6.959 calories/gm.-mole-°K. which introduces a negligibly small error of 0.07 per cent in the zero pressure heat capacity.

The heat capacity of the liquid, $C_{Sat.\ liq.}$, tabulated in Table 45 is fitted by the equation

$$C_p = 11.78 + 0.0147T \qquad (49)$$

The heat of vaporization at the normal boiling point, 90.19°K., is taken as 1630 calories/gm.-mole, the average of the three values in Table 39.

The triple point used is 54.363°K. as reported in Table 36.

The correction for gas imperfection, $- \frac{1}{R}\frac{dB}{dT}(p) + \frac{2B}{RT}(p)$, is obtained by plotting the second virial coefficients in Table 44 as a function of the absolute temperature, measuring the slope at the boiling point, and multiplying by the pressure. In this case the correction for gas imperfection is less than one calorie and is neglected.

Substituting in equation (59), we obtain the equation for the heat of vaporization of oxygen at the triple point

$$(\Delta H_s)_{t.p.} = 1630 + \int_{90.19}^{54.363} (6.959 - 11.78 - 0.0147T)dT + 0 \qquad (60)$$

which reduces to

$$(\Delta H_v)_{t.p.} = 1841 \text{ calories/gm.-mole} \qquad (61)$$

The heat of sublimation of oxygen at the triple point, $(\Delta H_s)_{t.p.}$, is calculated from the following relationship

$$(\Delta H_s)_{t.p.} = (\Delta H_v)_{t.p.} + (\Delta H_f)_{t.p.} \qquad (62)$$

where

$(\Delta H_f)_{t.p.}$ = the heat of fusion at the triple point

Substituting the value of $(\Delta H_v)_{t.p.}$ and $(\Delta H_f)_{t.p.}$ obtained from Table 39 in equation (62) we obtain a value of 1947 calories/gm.-mole for $(\Delta H_s)_{t.p.}$.

With a value of $(\Delta H_s)_{t.p.}$ for oxygen calculated, we develop a vapor pressure equation for solid oxygen from the triple point at 54.363°K. to the first transition point at 43.8°K. in the manner previously discussed for the case of argon.

$$\log p(mm) = 12.3161 - 473.71/T - 2.0431 \log T \qquad (53)$$

Vapor Pressure Equations of Solids with Transitions Below the Triple Point.--The calculation of the vapor pressure of the solid oxygen from the first transition point at 43.8°K. to the second transition point at 23.9°K.

will be used to illustrate the method of developing vapor pressure equations for solids with transitions below the triple point.

We calculate the heat of sublimation of oxygen in its second solid form at the first transition point, 43.8°K., using equation (22)

$$(\Delta H_s)_{\text{trans. Sol II}} = (\Delta H)_{\text{trans.}} + (\Delta H_s)_{\text{trans. Sol. I}} \tag{22}$$

where

$(\Delta H_s)_{\text{trans. Sol II}}$ = heat of sublimation of Solid II at the transition point

$(\Delta H)_{\text{trans.}}$ = heat of transition of solid oxygen at 43.8°K. from Table 38, 177.6 calories/gm.-mole

$$(\Delta H_s)_{\text{trans. Sol I}} = (\Delta H_s)_{\text{t.p.}} + \int_{T_{\text{t.p.}}}^{T_{\text{trans.}}} (C_p^o - C_{p_{\text{sol I}}})dT$$

The zero pressure heat capacity, $C_p^o$, used is the mean value of 6.96 calories/gm.-mole between the triple point at 54.363°K. and the first solid transition point at 43.8°K. taken from Table 38.

The heat capacity of solid oxygen from Table 46 is essentially constant

$$C_p = 11.02 \tag{50}$$

The method of calculating the heat of sublimation of oxygen at the triple point, $(\Delta H_s)_{\text{t.p.}}$, was shown in the previous section on sample cal-

culations to be 1947 calories/gm.-mole.

Substituting in equation (22) we obtain

$$(\Delta H_s)_{\text{trans. Solid II}} = 177.6 + 1947 + \int_{54.363}^{43.8} (6.96 - 11.02)dT \qquad (63)$$

which reduces to 2168 calories/gm.-mole for $(\Delta H_s)_{\text{trans. Solid II}}$.

The logarithm of the vapor pressure at the transition point, 43.8°K., obtained from the vapor pressure equation developed for the range 54.363°K. to 43.8°K. is taken as log $p_o$ in equation (15) and is equal to -1.8529.

The mean value of the zero pressure heat capacity, $C_p^o$, is obtained from Table 40 and is equal to 6.962 calories/gm.-mole-°K.

The heat capacity data in Table 46 are fitted by equation (51).

$$C_p = - 2.58 + 0.311T \qquad (51)$$

Substituting these values and the value of $(\Delta H_s)_{\text{trans. Solid II}}$ for $(\Delta H_s)_{\text{t.p.}}$ in equation (15) and integrating, we obtain the vapor pressure equation for solid oxygen from 43.8°K. to 23.9°K.

$$\log p(\text{mm}) = 1.9703 - \frac{447.50}{T} + 4.8018 \log T - 0.03398T \qquad (54)$$

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